Engineering Design File

PROJECT NO. 22901

Design Data for VOC Control for the TSF-09/18 V-Tank Remedial Action

INEEL

**Idaho National Engineering
and Environmental Laboratory**

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1. Title:	Design Data for VOC Control for the TSF-09/18 V-Tank Remedial Action

2. Index Codes:

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3. NPH Performance Category: _____ or ☒ N/A

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5. Summary:

This EDF provides flows and concentration for the design of a granular activated carbon (GAC) system for the V-Tank remediation offgas system. INEEL process engineering estimates of GAC based on approximate methods is commensurate with the vendor supplied estimates of 195 lb per sparged tank. Air stripping calculations provide an estimated stripping rate and average concentration assumed over a 42 hr period. Also, estimated concentrations for PCE, TCA, and TCE over time are provided, and carbon bed change-out frequencies are estimated. Numerical and analytical modeling show that there will be no immediate breakthrough and that the vendor estimates accurately predict performance. Preliminary estimates of GAC loading and comparison of gas emissions to industrial hygiene limits are included.

6. Review (R) and Approval (A) and Acceptance (Ac) Signatures:
(See instructions for definitions of terms and significance of signatures.)

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ACRONYMS

AEA	AEA Technologies
DCB	Dichloroethylene
DF	Decontamination factor
ER	environmental remediation
ES-CO/R/S	ex situ chemical oxidation/reduction/stabilization
GAC	granular activated carbon
IDLH	Immediate danger to life and health
KI-GAC	Potassium iodide impregnated GAC
MTZ	Mass transfer zone
NIOSH	National Institute for Occupational Safety and Health
ORNL	Oak Ridge National Laboratory
OU	operable unit
PCE	Perchloroethylene
RI/FS	Remedial Investigation/Feasibility Study
SCFM	standard cubic feet per minute
STEL	Short Term Exposure Limit
SVOC	Semi-volatile organic compound
TCA	Trichloroethane
TCB	Trichlorobenzene
TLV	Threshold limit value
TWA	Time weighted average
VOC	Volatile organic compound

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NOMENCLATURE

See also Appendices A and B

C   concentration of target solute in liquid, mg/liter

$k_p a$ mass transfer coefficient, min^{-1}

v   interstitial fluid velocity, cm/min

q   concentration of target solute in sorbent, mol/ml

q*   the concentration of the target solute in the solid phase at equilibrium with the liquid phase concentration, C, mol/ml

t   time, minutes

z   distance from column inlet, cm

ε   porosity, dimensionless

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1. SCOPE

The scope of this document includes: (1) Determine appropriate parameters including concentrations and rates for the implementation of granular activated carbon (GAC) for the V-Tank remediation off-gas system; (2) Provide comparisons to industrial hygiene limits for volatile organic carbon emissions (VOCs); (3) Provide modeling and estimated sizing of GAC for comparison to vendor estimates; and (4) Provide a conceptual model for flow for the different functions and estimate rates for GAC change-out frequency and number of units.

2. INTRODUCTION

An accelerated process for the destruction and/or removal of hazardous organic compounds from V-Tank liquids was previously determined to consist of ozonation plus sonication in recirculating flow systems (Ashworth 2004a, 2004b), a process considered to replace the originally proposed process (Fenton's Reagent oxidation). Since then, the equipment associated with a Fenton's Reagent chemical oxidation process at Oakridge National Laborator (ORNL) has become available that is commensurate with the original conceptual design for treating the V-Tank wastes (INEEL 2003). The sonication system would have been a method for accelerated destruction as the Fenton system was not available. However, the Fenton process current availability changed the scope of the treatment which changes previous sizing and specifications provided in EDF-4602, Rev. 0 (Ashworth 2004b). The scope of this EDF is to only determine parameters for an off-gas system and provide the concentrations, flows, and other information to designers (AEA Technologies) and vendors. This EDF also clarifies the mass transfer relationships and provides a better basis than what was provided in EDF-4602, Rev. 0.

3. BACKGROUND

The four stainless steel tanks (Figure 1) collectively known as the "V-Tanks" were installed at Test Area North (TAN) as part of the system designed to collect and treat radioactive liquid effluents from TAN operations. The V-Tanks are underground stainless steel tanks associated with Operable Unit (OU) 1-10. These four tanks are identified as Tanks V-1, V-2, V-3, and V-9. Tanks V-1, V-2, and V-3 are identical in shape and size. Tank V-9 is smaller and not shaped the same as the other tanks.

Tanks V-1, V-2, and V-3 were used for storage, while Tank V-9 was used as a primary separation tank to separate sediment and sludge from the liquid waste before transferring that waste to V-1, V-2, or V-3. Each of the V-Tanks currently contains a liquid and sludge layer, and all of the V-Tanks lack secondary containment. The tops of Tanks V-1, V-2, and V-3 are approximately 10 ft below grade, while the top of Tank V-9 is approximately 7 ft below grade. Tank V-9 is within Technical Support Facility (TSF) 18, while Tanks V-1, V-2, V-3, are within TSF-09.

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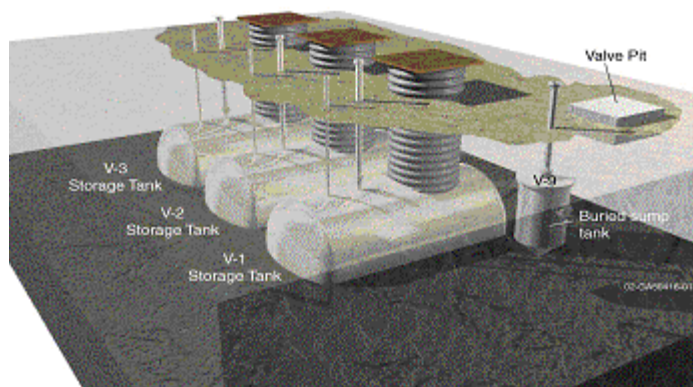
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Figure 1. V-Tank Isometric.

The V-Tanks and associated piping were installed in 1953 and became operational in 1958. The tanks were designed to collect and store liquid radioactive waste at TAN. The waste was stored in the underground tanks and then treated in the evaporator system located in TAN-616. Tanks V-1 and V-3 became inactive in the early 1980s. Tank V-2 was taken out of service in 1968 after a large quantity of oil was discovered in the tank; the oil was removed in 1981. In 1982, the excess free liquid was removed from the V-Tanks. Additional wastewater was reportedly added to Tank V-3 through 1985. Starting in 1985, all low-level radioactive waste at TAN was rerouted to the TAN-666 tanks through a piping modification in the TAN-1704 valve pit. The piping modification stopped intentional discharge to the V-Tanks in 1985. There is no evidence that sludge accumulating in the tanks was removed during or after site operations.

Tanks V-1, V-2, and V-3 are stainless steel tanks measuring 3 m (10 ft) in diameter, 5.9 m (19.5 ft) long, and buried approximately 3 m (10 ft) below ground surface (see Figure 2). The tanks have 50.8-cm (20-in.) manholes that are accessible through 1.8-m (6-ft) diameter culverts installed in 1981. Each tank is equipped with three subsurface influent lines and one subsurface effluent line. The tanks received radioactive wastewater via an influent line from Tank V-9. The remaining influent lines include a caustic line used to neutralize the waste prior to transfer to TAN-616 and a return flow line from the TAN-616 pump room. Tank V-3 has an additional inlet line from the TAN-615 east and west sumps. A single effluent line on each tank is routed to the TAN-616 pump room and evaporator system.

Liquid level measurements, recorded since April 1996, track the fluid levels in V-1, V-2, and V-3. Measurements since 1996, and anecdotal information preceding 1996, indicated an increase in the liquid level in Tank V-3 during the spring. This tank level stopped increasing in 2001. All lines, valves, and drains associated with the TSF-09 tanks are either plugged or identified as inactive; therefore, the increase is believed to be from spring snowmelt and runoff entering the tank through the manway above the entrance to Tank V-3. Liquid level measurements in Tanks V-1 and V-2 have remained relatively constant.

The volume of liquid and sludge in the V-Tanks has been estimated based on the results of the 1996 RI/FS sampling. Table 1 summarizes the capacities and current volumes (i.e., reflecting liquid level increases since the RI/FS) of the four V-Tanks.

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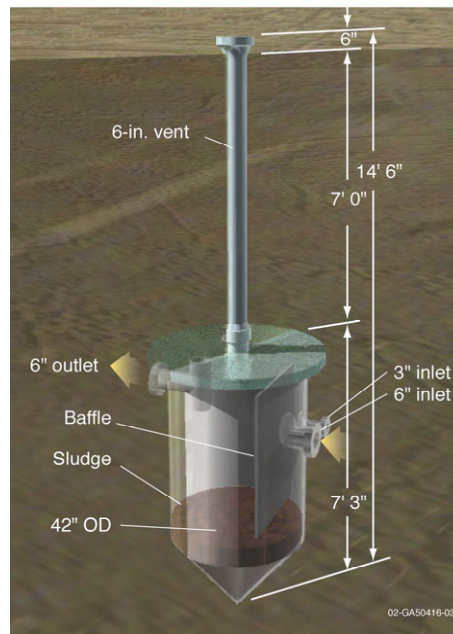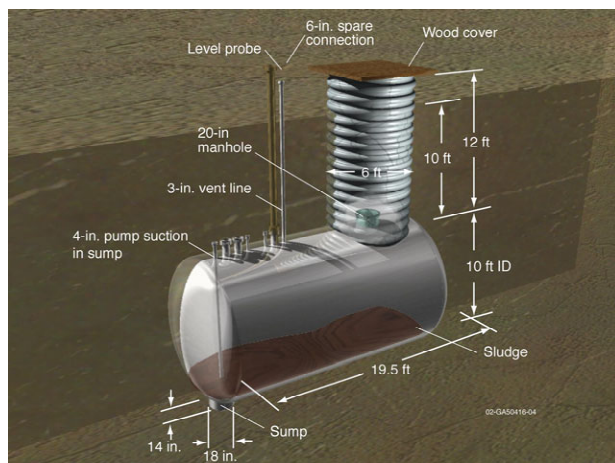
Figure 2. Tanks V-1, V-2, V-3, and V-9 (right).

Table 1. V-Tank Capacities and Current Contents (gallons).

Tank	Capacity	Sludge Mass (kg)	Sludge Volume	Liquid Volume	Total Volume
V-1	10,000	2,001	520	1,164	2,521
V-2	10,000	1,769	458	1,138	2,227
V-3	10,000	2,512	652	7,661	3,164
V-9	400	1,065	250	70	1,315
Total	30,400	7,348	1,880	10,033	11,913

A pre-conceptual design study addressed seven possible alternatives for remediating the V-Tanks and treating the contaminants. A subsequent Technical Evaluation study selected ex-situ chemical oxidation/reduction/stabilization (ES-CO/R/S) as the preferred remediation technology. Subsequently, a Vconceptual design report, Conceptual Design Report for Ex Situ Chemical Oxidation/Reduction and Stabilization of the V-Tanks at Waste Area Group 1, Operable Unit 1-10, INEEL /EXT-03-00438, June 2003, was written (INEEL 2003). The current waste treatment process is a Fenton Reagent, oxidation process, provided by AEA Technologies (AEA) to oxidize polychlorinated biphenyls (PCBs). A schematic of this process is shown in Figure 3. The basic process steps are discussed in 4.3 and the assumptions are discussed in 4.2. Requirements for the design are provided in the technical and functional requirements (INEEL 2000a/b).

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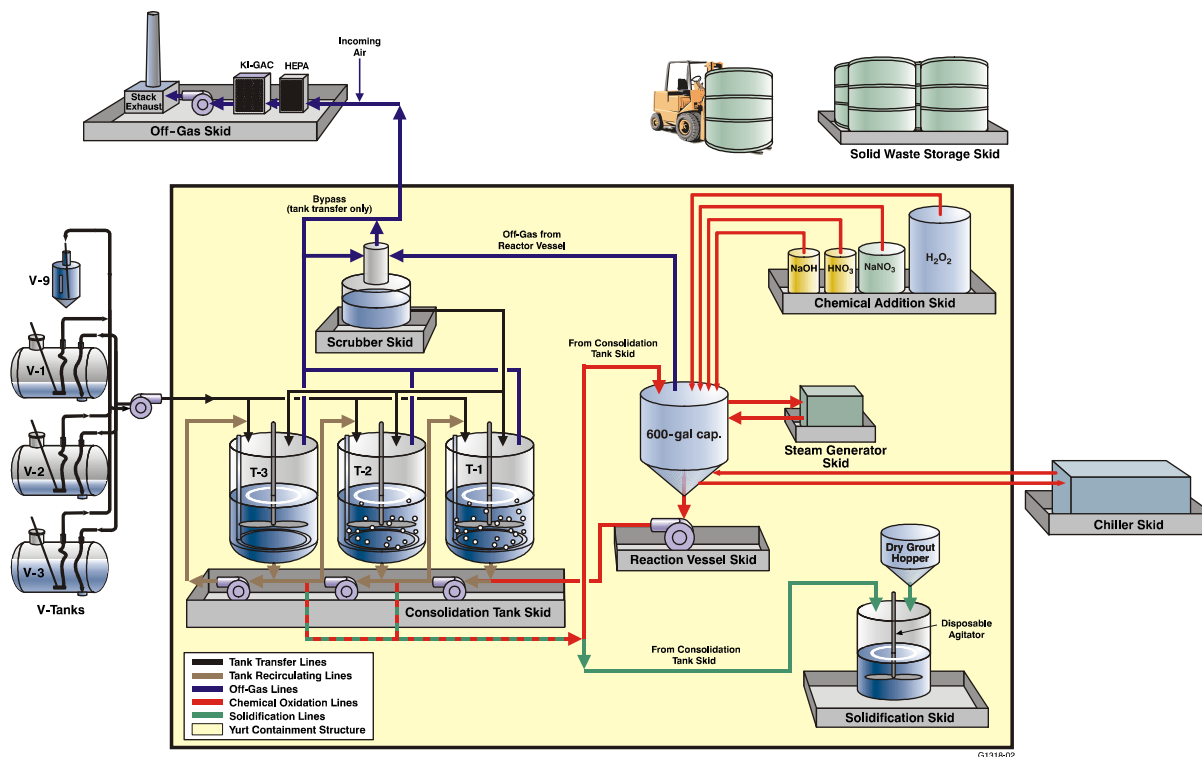
Figure 3. Process Schematic.

4. OFF-GAS SYSTEM

4.1 V-Tank Waste Characterization

To determine the applicable VOCs from the V-Tanks, the data from the characterization report (Tyson 2003) were used. However, this data needed to be filtered[a] to obtain weighted average concentrations and provide conservative estimates at the 90% confidence interval. The prescription used was to retain any component that had a "detect" in any tank in either phase. This filtering was done at the 90% confidence level with the detect values used for the tanks where detect values were listed (i.e., if one tank had an actual number where one or more of the other tanks had detect values, the detect values were averaged together with the actual numbers). This was done at the 90% confidence level using the Microsoft Excel function TINV (probability, degrees of freedom). The basic algorithm for filtering data is shown in Figure 4. As expected, this method provides conservative values for the component concentrations.

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a. Note that this EDF characterization will not match other documents due to the inherent conservatism.

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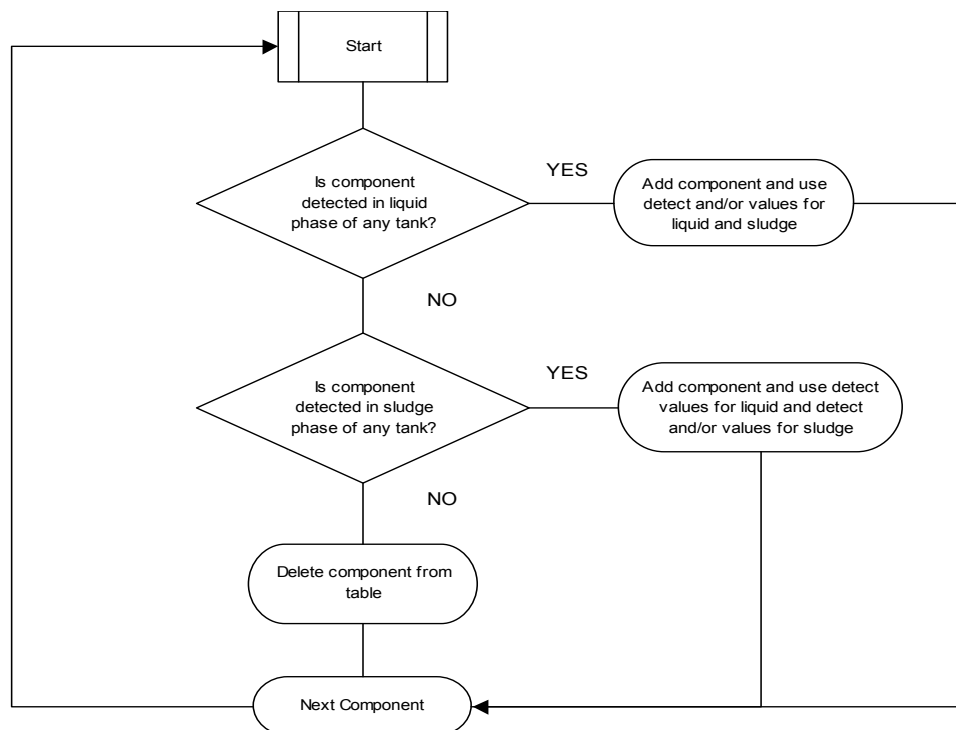
Figure 4. Characterization Flowchart.

Table 2. Miscellaneous Streams.

Waste Stream	Volume	Adjusted Volume gal	Rationale for Inclusion into V-Tank Treatment Unit
ARA 16	80 gallons	380	Agency agreement Waste stream similarity No designated treatment process
Unaltered V-tank samples	<50 gallons	50	Return of V-tank samples to point of origin
OU 1-07B sludges	4 gallons	15	CERCLA waste that originated form the V-tanks prior to injection well discharge and subsequent retrieval
Liquids removed from isolating piping form TAN-616 to V-1, V-2, V-3 and V-9	3 carboys (5-gal) 1 Drum (30-gal)	20	Waste was in V-tank feed lines

The results of this filter are provided in Tables 3, 4, and 5 for organic compounds, inorganics, and radionuclides[b] respectfully. The semivolatile organic compounds (SVOCs) in Table 2 were determined during the screening process in Appendix A. Again, note that the values in these tables are the 90% confidence levels, and so are higher than the measured levels, providing more conservatism in the design. The values in the " Total mg/L" column include both the amounts of contaminants dissolved in the water plus the amounts of contaminants from the sludge, per volume of water. While the concentrations and

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b. Some of the radionuclides had no values for V-9 so the highest from the set was used.

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masses of these contaminants vary in each of the V-tanks, the different concentrations are averaged (using weighted averages) when the V-tank contents are transferred to, and mixed in, the consolidation tanks. There will also be some small-volume, miscellaneous liquids added to the consolidation tanks for treatment (e.g., from ARA-16). The addition of these small streams is not expected to significantly change the characterization with the exception of the trichloroethane (TCA) from ARA-16. Since this had significant impact, it was weight-averaged into the characterization the V-Tank VOC profiles . Also, there are some compounds present in the miscellaneous liquids that are not part of the characterization (e.g., acetone) that were not included but will adsorb onto the GAC beds.

Table 3. Organic Compounds Based on Figure 1.

	Sludge (mg/kg)	Liquid mg/L liquid volume	Total[a] mgL liquid volume	Total Mass Sludge (kg)	Total Mass Liquid (kg)	Total Mass (kg)
VOCs						
Bromomethane	2.47E+01	1.65E-01	4.94E+00	1.81E-01	6.27E-03	1.88E-01
Chloroethane	9.56E+01	3.30E-01	1.88E+01	7.03E-01	1.25E-02	7.15E-01
Chloromethane	1.59E+01	5.66E-02	3.14E+00	1.17E-01	2.15E-03	1.19E-01
1,2-dichlorobenzene	6.95E+01	2.46E+00	1.59E+01	5.11E-01	9.34E-02	6.04E-01
1,3-dichlorobenzene	9.68E+01	2.52E+00	2.13E+01	7.11E-01	9.58E-02	8.07E-01
1,4-dichlorobenzene	1.03E+02	2.52E+00	2.24E+01	7.54E-01	9.58E-02	8.50E-01
1,1-dichloroethane	2.10E+01	9.69E-02	4.15E+00	1.54E-01	3.68E-03	1.58E-01
trans-1,2-dichloroethylene	3.52E+01	4.32E-01	7.23E+00	2.58E-01	1.64E-02	2.75E-01
methylene chloride	9.56E+01	6.05E-01	1.91E+01	7.03E-01	2.30E-02	7.26E-01
PCE	1.14E+03	3.50E-01	2.20E+02	8.34E+00	1.33E-02	8.35E+00
1,2,4-trichlorobenzene	9.81E+01	2.52E+00	2.15E+01	7.21E-01	9.58E-02	8.16E-01
TCA	5.99E+02	8.25E-01	1.03E+02	3.89E+00	3.13E-02	3.92E+00
TCE	4.61E+03	4.31E+00	8.97E+02	3.39E+01	1.64E-01	3.41E+01
vinyl chloride	4.71E+01	2.51E-01	9.37E+00	3.46E-01	9.53E-03	3.56E-01
					Total	5.20E+01
SVOCs						
Aroclor-1260	1.44E+02	2.53E-01	2.81E+01	1.06E+00	9.59E-03	1.07E+00
bis(2-ethylhexyl)phthalate	3.71E+03	1.54E-01	7.18E+02	2.72E+01	5.83E-03	2.73E+01
2,4-dimethylphenol	1.18E+02	2.52E+00	2.54E+01	8.70E-01	9.58E-02	9.66E-01
4,6-dinitro-2-metylphenol	5.98E+02	4.86E+00	1.21E+02	4.39E+00	1.85E-01	4.58E+00
di-n-octylphthalate	1.20E+02	2.52E+00	2.57E+01	8.81E-01	9.58E-02	9.76E-01
2-methylnaphthalene	3.31E+01	2.52E+00	8.92E+00	2.43E-01	9.58E-02	3.39E-01
2-methylphenol	1.38E+02	2.53E+00	2.93E+01	1.02E+00	9.61E-02	1.11E+00
4-methylphenol	1.18E+02	2.53E+00	2.54E+01	8.67E-01	9.61E-02	9.63E-01
Naphthalene	9.20E+01	2.52E+00	2.03E+01	6.76E-01	9.58E-02	7.72E-01
4-nitrophenol	5.98E+02	4.86E+00	1.21E+02	4.39E+00	1.84E-01	4.58E+00
Phenol	1.02E+02	2.52E+00	2.22E+01	7.46E-01	9.58E-02	8.42E-01
Pyrene	1.20E+02	5.87E-01	2.38E+01	8.81E-01	2.23E-02	9.03E-01
					Total	4.43E+01
TOC	1.18E+05	6.28E+01	2.29E+04	8.66E+02	2.39E+00	8.68E+02

a. The total refers to the mass in both phases divided by the liquid volume.

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Table 4. Inorganic Compounds Based on Figure 1[a]

	Sludge mg/kg	Liquid mg/L liquid volume	Total mg/L liquid volume		Sludge mg/kg	Liquid mg/L	Total mg/L
	Inorganic Components, Cations				Inorganic Components, Anions[c]		
Al	4.05E+03	8.10E-01	7.85E+02	Sb	8.91E+00	2.23E-01	1.95E+00
Ba	1.48E+02	4.56E-01	2.91E+01	As	3.83E+00	1.47E-02	7.55E-01
Be	8.36E+00	5.33E-02	1.67E+00	B	1.79E+01	1.26E+01	1.61E+01
Ca	9.86E+03	4.84E+01	1.96E+03	Br	9.55E+00	2.68E+00	4.53E+00
Cd	1.92E+01	3.38E-02	3.75E+00	Cl	1.63E+02	1.28E+02	1.59E+02
Co	2.21E+00	8.53E-02	5.13E-01	Cr	2.44E+03	8.81E-02	4.72E+02
Cu	1.41E+02	7.67E-02	2.73E+01	F	5.69E+00	1.17E+01	1.28E+01
Fe	2.25E+04	1.81E+00	4.35E+03	Nitrate	7.72E+00	9.92E-01	2.48E+00
Mg	1.32E+04	2.28E+01	2.57E+03	Nitrite	5.69E+00	9.37E+00	1.05E+01
Mn	6.33E+03	1.20E+00	1.23E+03	Phosphate	7.15E+00	5.65E+00	7.03E+00
Pb	2.93E+02	1.80E-01	5.69E+01	P	6.03E+04	1.42E+00	1.17E+04
Hg	5.57E+02	5.05E-02	1.08E+02	Se	3.65E+00	1.63E-02	7.22E-01
Ni	1.30E+02	3.92E-01	2.55E+01	Si	1.01E+05	9.64E+00	1.95E+04
K	2.45E+03	1.69E+02	6.42E+02	Sulfate	2.49E+02	2.37E+01	7.19E+01
Ag	1.38E+02	1.18E-02	2.67E+01				
Na	7.13E+02	2.79E+02	4.17E+02				
Tl	2.37E+01	1.61E-02	4.61E+00				
Sn	1.40E+01	2.08E-03	2.70E+00				
V	2.28E+00	1.13E-01	5.53E-01				
Zn	1.40E+03	7.88E+00	2.79E+02				

a. The charge balance for the cations and anions in Table 4 indicates that additional, uncharacterized anions, not shown in Table 4, are present (Ashworth 2004b). The uncharacterized anions may be HCO_3^-.

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Table 5. Radionuclides Based on Figure 1.

	Sludge (Ci/kg)	Liquid Ci/L liquid volume	Total Ci/L liquid volume
Radionuclides			
Pu-238	1.83E-05	1.50E-09	3.55E-06
Pu-239/240	7.37E-06	4.34E-10	1.43E-06
Am-241	9.51E-06	3.83E-10	1.84E-06
Cm-242	4.86E-08	2.33E-11	9.43E-09
Cm-243/244	2.52E-06	6.49E-11	4.88E-07
Np-237	3.58E-08	8.83E-11	7.01E-09
U-233/234	5.89E-06	1.98E-08	1.16E-06
U-235	1.91E-07	6.52E-10	3.76E-08
U-238	8.01E-08	2.05E-10	1.57E-08
Sr-90	1.58E-02	1.24E-05	3.07E-03
Ag-108	1.28E-06	3.93E-09	2.52E-07
Ag-110	2.39E-06	6.74E-09	4.69E-07
Ce-144	1.73E-05	3.91E-08	3.38E-06
Co-58	2.44E-06	6.84E-09	4.78E-07
Co-60	4.81E-04	2.40E-08	9.31E-05
Cs-134	1.45E-06	1.54E-09	2.82E-07
Cs-137	8.08E-03	7.36E-06	1.57E-03
Eu-152	2.60E-05	1.03E-08	5.05E-06
Eu-154	3.66E-05	3.48E-09	7.09E-06
Eu-155	4.23E-06	1.36E-08	8.32E-07
Mn-54	8.76E-07	2.51E-09	1.72E-07
Nb-95	5.78E-06	7.46E-09	1.13E-06
Ra-226	4.17E-06	5.01E-09	8.11E-07
Ru-103	2.13E-05	5.35E-08	4.17E-06
Ru-106	1.75E-05	4.64E-08	3.43E-06
Sb-125	7.09E-06	1.97E-08	1.39E-06
Zn-65	2.19E-06	5.57E-09	4.30E-07
Zr-95	5.16E-06	1.33E-08	1.01E-06
I-129	9.13E-08	7.60E-10	1.84E-08
Ni-63	1.29E-03	2.79E-07	2.51E-04
H-3	0.00E+00	2.53E-05	2.53E-05

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4.2 Assumptions and Uncertainties

- The sparging includes 52 kg of VOCs but does not include the 42 kg of SVOCs or the TOC (assumed to consist of cutting oil, etc).

- It is assumed that the liquid-phase mass transfer coefficient ($k_L a$) from Perry's Handbook (Perry and Green 1984) applies to air stripping this particular waste. There is an uncertainty associated with this assumption as no actual testing will be done. However, the literature[d] indicates that the mass transfer coefficient $k_L a$ is in fact on the order suggested, and the solid-liquid transfer resistance of contaminants in the sludge to the supernate is small compared to the predicted $k_L a$.

- Stripping of essentially all of the VOC components from the consolidation tanks during air sparging can take several days. However, the sparge duration to strip essentially all of the PCE, TCA, and TCE is predicted to be 42 hours/tank, based on the longest estimated sparge duration (for TCE). Dichlorobenzene, having a low Henry's law constant, takes much longer and, if there really is a significant quantity, much of it would remain after sparging[e] for only 42 hours. However, dichlorobenzene is not present in significant amounts compared to PCE, TCA, and TCE, and the estimated small amount of total dichlorobenzenes is based on detection limit values. Actual levels of dichlorobenzenes, and other species, in the V-Tanks are probably lower than estimated in Table 2.

- During sparging, the more volatile components will volatilize out of the liquid faster, at higher concentrations in the air. The VOC concentrations in the sparge air will decrease as the VOCs in the liquid become more depleted. Also, without testing, if the mass transfer coefficient $k_L a$ is much lower than the literature suggests, it could take longer than 42 hours to strip the VOCs. However, the literature indicates that it will be faster rather than slower.

- The dilution air from the V-Tanks and from displacement filling of the consolidation tanks have zero VOC concentrations (i.e., the headspace displacement as the liquid level rises). This should have little impact, if wrong, as the presence would increase the concentration.

- It is assumed that the decontamination factor (DF) across the GAC bed is 200 for all components, when the GAC bed depth is 12 inches, the superficial velocity in the GAC bed is 2 ft/s, and the superficial residence time in the GAC bed is 0.5 second[f]. This is based on the vendor estimate of 99.5% removal for mercury under similar GAC bed operating conditions. If this assumption is incorrect, the threshold limit value-time weighted average (TLV-TWA) could be exceeded but it would require a DF < 3 for TCE measured at the stack discharge. The immediately dangerous to life and health (IDLH) values should not be exceeded even if the assumption is wrong for any of the components.

- The vendor capacity average for adsorption is 48%. If the actual was 10%, the amount of carbon would be approximately five times greater.

- If there is significant evolution of gaseous organic compounds during step 3, additional carbon will be needed.

- The air in-leakage to the consolidation tanks is assumed to be 1 scfm.

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d. See Appendix B.

e. Dichlorobenzene and some others are artifacts of the characterization prescription and are questionable as to their presence.

f. This is the vendors (Flanders filters) design for the system.

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- The average VOC sorption capacity for the GAC is 48 wt% (0.48kg sorbed VOCs per kg virgin GAC) based on vendor estimates. The relative humidity of the VOC-laden air may be high enough to reduce the VOC sorption capacity of the GAC below the assumed capacity. If so, then the estimated GAC bed change-out frequency will need to be increased to avoid GAC bed depletion and loss of VOC sorption efficiency.. This could be exacerbated by the higher concentrations of gas VOCs during initial sparging. However, the heater on the off-gas skid will control humidity.

- Radiological emissions in the ventilation, sparge, and process air will be low enough so that only a single high efficiency particulate air (HEPA) filter still provides sufficient control of radionuclide emissions.

- Spent carbon from the carbon bed, that will contain sorbed VOCs and potentially some radionuclide contamination, can be replaced as frequently as necessary during the remedial action, and can be disposed of safely and at reasonable cost at Envirocare (or other permitted facility if treatment is required) or the INEEL CERCLA Disposal Facility (ICDF).

4.3   Off-gas System Conceptual Model

The conceptual model for the remedial action off-gas system is shown in Figure 5, Figure 6, and Figure 7. The remedial action will include 3 separate steps or phases during which VOC, PCB (semi-volatile organic carbon or SVOC), Hg, and radionuclide emissions must be controlled:

- Transfer of V-Tank Contents to the Consolidation Tanks

- Consolidation Tank Sparging

- ExSitu Chemical Oxidation/Reduction.
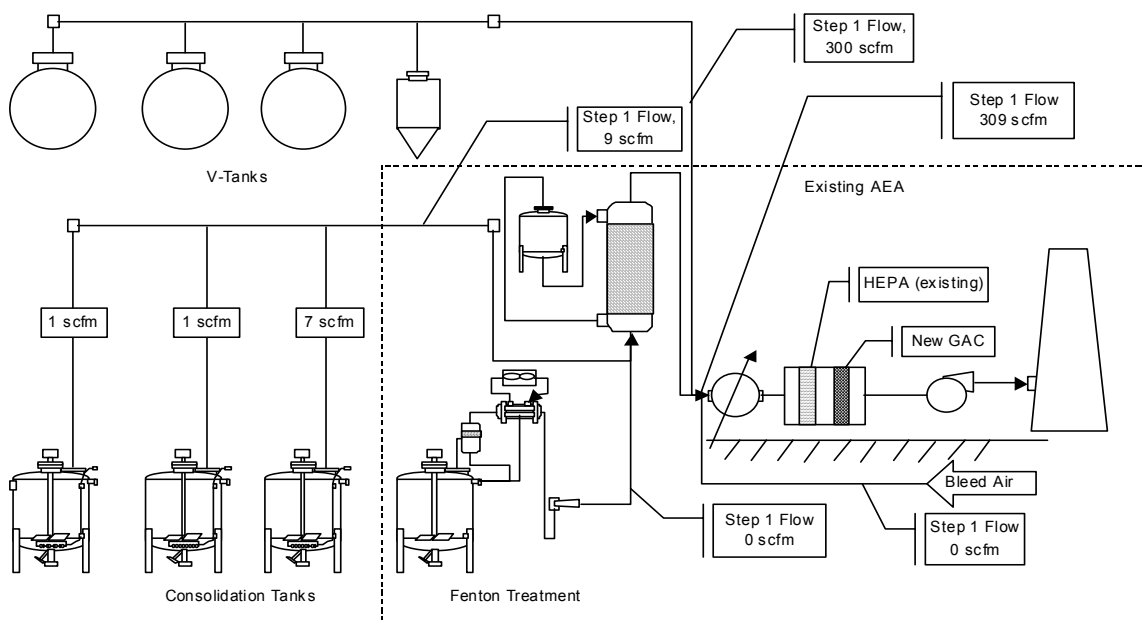
Figure 5. Gas Treatment Schematic, Step 1, Consolidation.

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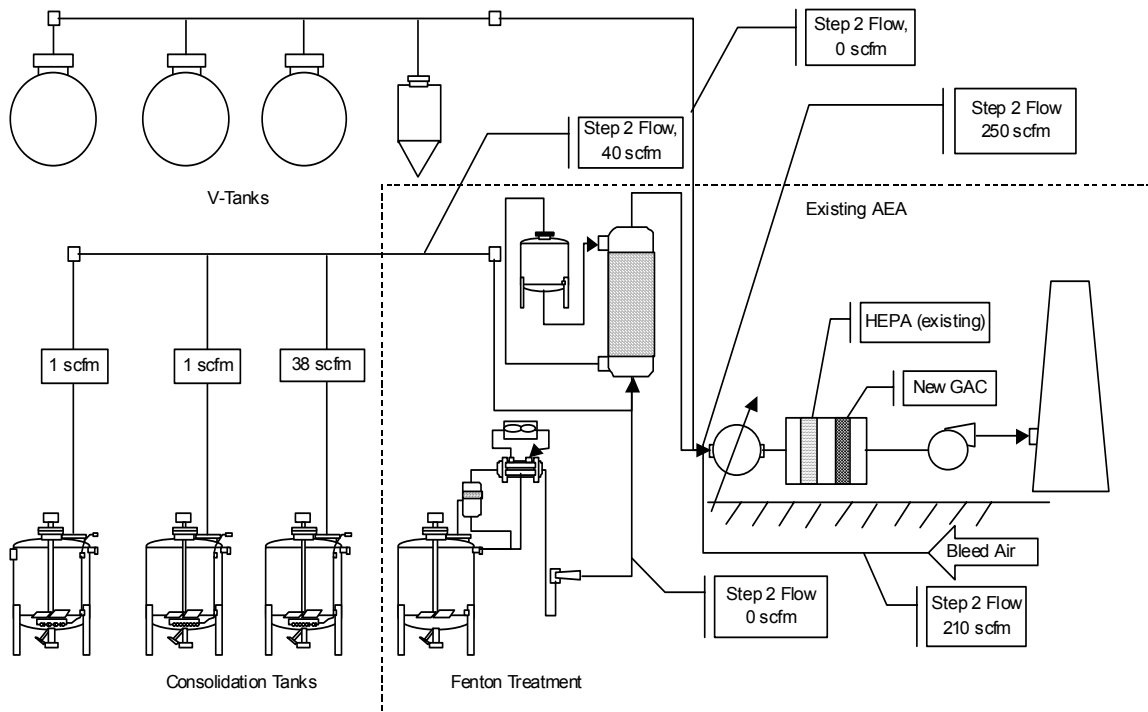Revision 0
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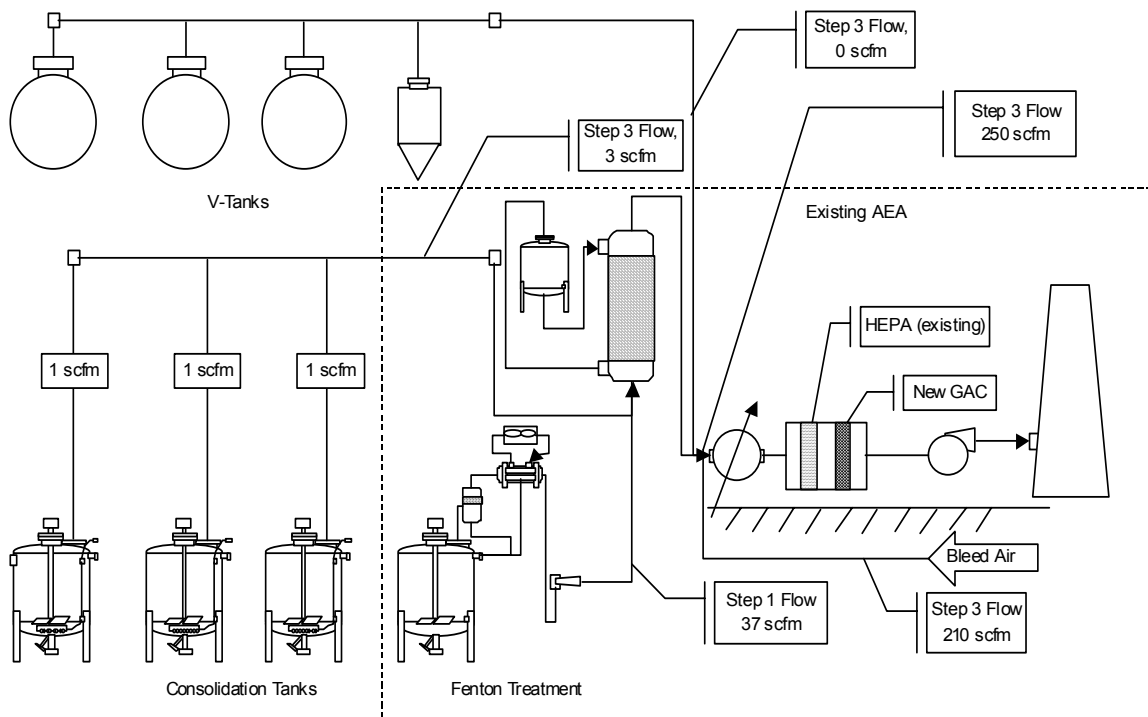Figure 6. Gas Treatment Schematic, Step 2, Mixing/Sparging.

Figure 7. Gas Treatment Schematic, Step 3, Oxidation/Treatment.

The V-tanks and the consolidation tanks will be ventilated to the off-gas system to maintain slightly negative pressure (about –5 inches water) in all tanks as they are filled, treated, or emptied. The

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off-gas system consists of ventilation ducting from the V-Tanks, the consolidation tanks, and the chemical oxidation/reduction vessel, and skid-mounted offgas system components. The chemical oxidation/reduction vessel and off-gas system components are existing components mounted on skids originally provided by AEA Technologies (AEA) that will be provided for the V-Tank remedial action.

The equipment includes control equipment designed for the AEA oxidation/reduction vessel. The system includes, the chemical oxidation/reduction vessel, a condenser, a demister, and a scrubber. The condenser, demister, and scrubber are designed to operate at about 125°F to condense and return water from the vessel offgas back to the vessel, and to provide scrubbing of any residual particulates, acid gases, and aerosols in the vessel offgas. Asecond skid includes a heat exchanger, two HEPA filters in series in a HEPA filter housing, the induced draft (ID) fan, and a close-coupled stack. The HEPA filters and ID fan were designed for an air flowrate of 1,000 scfm.

This equipment does not include a fixed carbon bed, considered necessary for the V-Tank remedial action for controlling VOCs and Hg. While separate off-gas control systems, one for each step of the remedial action, were considered, the current conceptual design includes simply modifying the equipment as needed to provide sufficient control of organic and Hg emissions, and also to provide for appropriate system air flowrates. The HEPA filter system and induced draft fan will provide draft and final HEPA filtration for all three steps. These modifications will include:

- Tee in the consolidation tank ventilation duct just upstream of the scrubber

- Tee in the V-Tank ventilation duct just downstream of the scrubber

- Addition of the ability to add bleed air for flow rate control upstream of the heat exchanger (bleed air added just upstream of the ID fan would provide for more efficient particulate matter, radionuclide, VOC, and Hg control, but is not considered possible considering the equipment configuration)

- Replacement of the second HEPA filter with a fixed carbon bed in the HEPA filter housing

- Dampening the nominal design flowrate of 1,000 scfm to values, including the bleed air, appropriate to each step of the remedial action and appropriate for efficient carbon bed operation.

The consolidation tank ventilation duct will be teed into the off-gas system just upstream of the scrubber, so that the scrubber can provide some removal of aerosols in the sparge air from the consolidation tanks. Removing these aerosols upstream of the reheater and the HEPA filters increases the HEPA filter life. Since the sparge air temperature will be near ambient temperature, passing the sparge air through the condenser (which was designed to condense water from hot, ~100°C water vapor-laden gas from the oxidation/reduction vessel) was not considered necessary.

Compared to the sparge air from the consolidation tanks, the ventilation air from the V-Tanks will contain less aerosols and probably will not be at its dewpoint. Scrubbing the ventilation air prior to reheating and HEPA filtration was not considered necessary. The V-Tank ventilation air duct was therefore teed into the off-gas system just downstream of the scrubber, and upstream of the reheater and HEPA filters.

Bleed air for total gas flow rate control will be added just upstream of the heat exchanger. Since the ID fan is designed for 1,000 scfm flow rate, the maximum reasonable turndown of about 4:1 results in a minimum ID fan flow rate of about 250 scfm. Considering reheater, HEPA filter, and carbon bed performance, this location is not as good as adding the flow control air downstream of the carbon bed and

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upstream of the fan. The downstream location would enable gas flow rates of only about 40 scfm for steps 2 and 3. This lower flowrate would afford more efficient HEPA filter and carbon bed performance, at the same time as the highest performance is needed when aerosol, particulate, VOC, and Hg emissions from the treatment processes will be highest. At a lower face velocity and higher initial particulate matter concentrations the HEPA filter will be more efficient. The carbon bed efficiency and loading will also be higher at higher initial VOC and Hg concentrations, a lower gas velocity, higher gas residence time, and shorter mass transfer zones. However, space may not be sufficient to tee in the flow control air between the carbon bed and the ID fan. Furthermore, the HEPA filter pressure drop instrumentation, needed for HEPA filter process control, is not sensitive enough to accurately monitor the HEPA filter differential pressure at flowrates as low as 40 scfm. For these two reasons, the flow control bleed air will be teed into the skid upstream, not downstream, of the reheater, HEPA filter, and carbon bed. Even at the higher flowrates, the reheater, HEPA filter, and carbon bed are expected to adequately control particulate matter, radionuclides, VOCs, and Hg.

Several options were considered to provide VOC and Hg control during the remedial action. VOC control options included thermal oxidation, condensation, and sorption (DOE 2002, INEEL 2002). The initial off-gas system conceptual design for the initial ex situ chemical oxidation, reduction, and stabilization design included fixed bed activated carbon sorption for VOCs and Hg (Raivo 2003).

After the first conceptual design was prepared, the treatment system conceptual design was modified to enable the use of the available AEA system. While the initial carbon bed design included redundant carbon beds that were sized for the entire estimated VOC and Hg loading during the remedial action, these could not be incorporated into the AEA skid. The space limitations of the AEA skid restricted the carbon bed design. The second HEPA filter will be replaced with a fixed carbon bed in the HEPA filter housing. The maximum size for the carbon bed is 2×2 ft (4 ft^2) cross-section area, with a 1 ft bed depth. The bed superficial volume is 4 ft^3. The mass of carbon in this volume is about 65 lb of GAC (Flanders Filters) since not all of the volume is occupied by GAC. However, the depth normal to flow is 12 in. The minimum residence time for efficient VOC and Hg control is, according to the vendor, only a 0.25 s residence time[g].

The new carbon bed system, designed for installation downstream of the HEPA filter and upstream of the ID fan, will control emissions of organic compound and Hg emissions during all three steps of the remedial action. The carbon bed will contain a mixture of regular GAC for VOC control, and potassium iodide impregnated GAC (KI-GAC) to remove Hg. This design requires multiple carbon bed changeouts during the remedial action. For each changeout, the treatment process must be stopped for the duration of the changeout to prevent uncontrolled VOC and Hg emissions.

4.3.1   Transfer of V-Tank Contents to the Consolidation Tanks

The first step of the remedial action is to transfer the contents of the V-Tanks to the consolidation tanks. This transfer will be done by first transferring the Tank V-3 supernatant to one of the consolidation tanks for later use in flushing other tanks. Then each of the other V-tanks will be pumped to one of the other consolidation tanks, and flushed with Tank V-3 water.

During the first step of the remedial action, the total air flow rate from the consolidation tanks totals about 9 scfm – an assumed in-leakage of 2 scfm, plus the air displacement rate from liquid being pumped to a filling tank, 7 scfm. The air flow rate from the V-Tanks is estimated at 300 scfm based on the assumption that the manway for one of the V-tanks is open, and the calculated air flowrate of

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g. The residence time for this unit will be 4 ft^3/250 ft^3/min = 0.96 s based on empty bed.

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300 scfm recommended to maintain a face velocity of 140 f/m in the open manway for contamination control.

4.3.2   Consolidation Tank Sparging

In step 2 of the remedial action, the consolidation tanks are equalized by pumping into two tanks, saving the third tank for treated liquid from the ES-CO/R/S process. Initially, there will be supernatant from Tank –V-3 in one tank and mainly sludge in another. The two tanks will be sparged consecutively for 42 hr each at approximately 38 scfm to remove 99% or more of the total mass of all VOCs and most of the volatile mercury in each tank.

The design total off-gas flow rate for step 2 is 250 scfm, based on the minimum reasonable flowrate for the induced draft (ID) fan and maximum reasonable superficial air velocity and flowrate through the carbon bed. This flowrate represents a 4:1 turndown for the ID fan, which is sized for 1,000 acfm. This flowrate is the sum of about 1 scfm air inleakage for each consolidation tank not being sparged, a sparge flowrate of about 38 scfm for the tank that is being sparged, zero air flow from the V-Tanks, and a bleed air flowrate of about 210 scfm. The bleed air is necessary to increase the process air flowrate from about 40 scfm to the minimum design value for the fan.

4.3.3   ExSitu Chemical Oxidation/Reduction

The last step, step 3, of the remedial action is the oxidation/reduction process that uses Fenton's reagent to destroy PCBs (SVOCs) via free radical oxidation. Following sparging, the water with suspended sludge is transferred from the consolidation tanks to the reaction vessel for this stage. During this process at the solution boiling point, intermediate VOCs are formed and these, along with the remaining total VOCs left in the waste from step 2, are emitted to the off-gas from the reaction vessel. For design purposes, 1% of the total VOCs are assumed to remain in the waste following the sparging step.

The total off-gas flow rate during step 3 is also set at 250 scfm, the minimum reasonable air flow rate for the ID fan. This flow rate is the sum of about 3 total scfm air inleakage from the consolidation tanks, zero air flow from the V-Tanks, 37 scfm from the chemical oxidation/reduction vessel, and about 210 scfm bleed air (the actual flow will be less during the process but the maximum scrubber rate is 40 scfm. The 37 scfm plus the 3 scfm in-leakage from the consolidation tanks leads to 40 scfm).

4.4   Calculations of VOC Concentrations in the Off-gas

There are several mechanisms for VOC emissions into the gas phase. These are described below. The calculations are provided in Appendices A and B.

The design is based on replacing the second HEPA unit from the AEA off-gas skid with KI-GAC. This is shown in Figure 8. The process off-gas mixes with the bleed in flow rate control air and is heated to reduce the relative humidity. The gas is filtered via the HEPA followed by VOC and Hg removal in the KI-GAC unit, a $2 \times 2 \times 1$ ft rectangular box containing approximately 65 lb GAC impregnated with KI (2%). The gas passes through the blower to the stack. VOC monitoring at the stack (described in Appendix C) will be performed using access ports on the stack. Alternatively, hand-held monitors for VOCs and mercury can be used during GAC change-outs.

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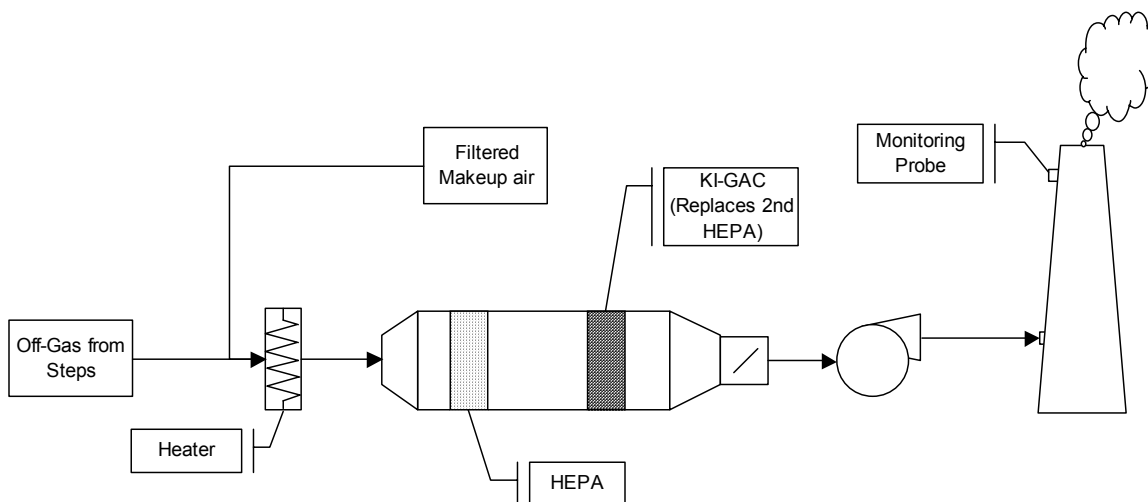
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Figure 8. GAC System Design.

- During consolidation tank filling operations (step 1), vapors from the liquid will be emitted as part of the vented gas stream from the ventilated V-tanks and from the consolidation tanks. Negligible VOC emissions are assumed in the ventilation air from the V-tanks. The concentrations of contaminants in the consolidation tank ventilation air are conservatively assumed to be in equilibrium with the concentrations of those contaminants in the water, according to Henry's Law. The gas flow rate from the V-tanks is assumed to be 300 scfm. The gas flow rate from the consolidation tanks is assumed to be 9 scfm. The total flow rate including in leakage and displacement is approximately 309 scfm. The estimated vapor phase concentrations downstream of where these air streams are combined are based on Henry's Law assuming that the 300 scfm flow, and the 1 scfm assumed in-leakage flows are basically zero concentration, and the VOCs and Hg all come from the displacement. The result is shown in Table 6 as step 1.

- VOC emissions during step 2 are estimated assuming that the V-Tank ventilation air flow rate is zero and that there is a 38 scfm sparge rate in one of the consolidation tanks plus the 2 scfm air leakage from the other two. The rate of VOC mass transfer (from Perry 1984) is used to estimate the VOC concentrations in the consolidation tank sparge air. Since this is a batch air stripping operation, the highest vapor concentration will occur at time zero and decrease thereafter to zero. Only a few of the VOCs, those present at the highest concentrations in the V-Tanks, were considered in the sparging calculations. These were PCE, TCA, TCE, and TCE. TCE was the worst-case VOC of concern as it required the longest sparge time to obtain approximately 99% removal. Calculations in Appendix A shows that even TCE is nearly quantitatively stripped from the consolidation tanks by sparging for 42 hours. Trichlorobenzene (TCB) requires much more time to strip according to the model primarily based on its low Henry's constant and the approximate average solid-liquid partition coefficient used, but is present in the V-Tanks at much lower concentrations compared to PCE, TCA, and TCE. Potential errors in reported PCE, TCA, and TCE concentrations in the V-Tanks were included in the Appendix A calculations. Based on their much higher volatilities, these are easily removed within the sparge time according to predictions. The air concentrations of PCE, TCA, and TCE during steps 1 and 2 of the remedial action are shown in Table 6.

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Table 6. Raw and Dilute Concentrations, Retrieval/Sparge.

	Step 1		Step 2	
Flow, scfm	7	309	38	250
Temperature, °C	25	25	25	25
Humidity (RH)	100	100	100	100
VOCs, ppm$_v$	Raw	Dilute	Raw	Dilute
Bromo methane	12	0.27	10	2
Choloro ethane	59	1.29	59	9
Chloro methane	10	0.21	13	2
1,2-dichlorobenzene	35	0.75	22	3
1,3-dichlorobenzene	64	1.38	29	4
1,4-dichlorobenzene	82	1.77	31	5
1,1-dichloroethane	6	0.13	8	1
1,2-dichloroethylene	36	0.77	15	2
methylene chloride	20	0.44	45	7
PCE	33	0.71	267	41
TCA	96	2.09	32	5
1,2,4-trichlorobenzene	34	0.74	115	17
TCE	332	7.18	1376	209
Vinyl Chloride	84	1.81	30	5
Mercury	2	0.05	109	17

- During free-radical destruction of PCBs and other SVOCs not volatilized during sparging via Fenton's reagent (step 3) in the batch reaction tank, there are likely intermediate degradation products that will volatilize via evaporating mass transfer. Accurately characterizing and quantifying these products is not possible. However, the accumulation will depend on the rate of formation, rate of destruction, and rate of mass transfer[h]. The maximum gas flow rate from the reaction vessel during step 3 is 40 scfm. However, the concentrations of the vapor phase VOCs produced will be determined by AEA. Any evolution of vapors from step 3 is not accounted for in this EDF noting that the component concentrations of VOC byproducts are much lower than the intial VOC concentrations based on the initial SVOC concentrations.

Table 6 shows the average estimated VOC and Hg concentrations in the off-gas during steps 1 and 2. The raw concentrations in Table 6 indicate the concentrations upstream of where the off-gas from the consolidation tanks is diluted by the V-Tank ventilation air (in step 1) or the bleed in flow control air (in step 2). The dilute concentrations in Table 6 indicate the concentrations diluted by the V-Tank air or the flow control air. The step 2 concentrations are averaged over a 42 hour sparge time. The actual VOC and Hg concentrations are time dependent and are far higher at first and are predicted to strip off rapidly as shown in Figure 9.

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h. The k_G is derived from the J-Factor for evaporating mass transfer (see Nomenclature for symbol definitions).

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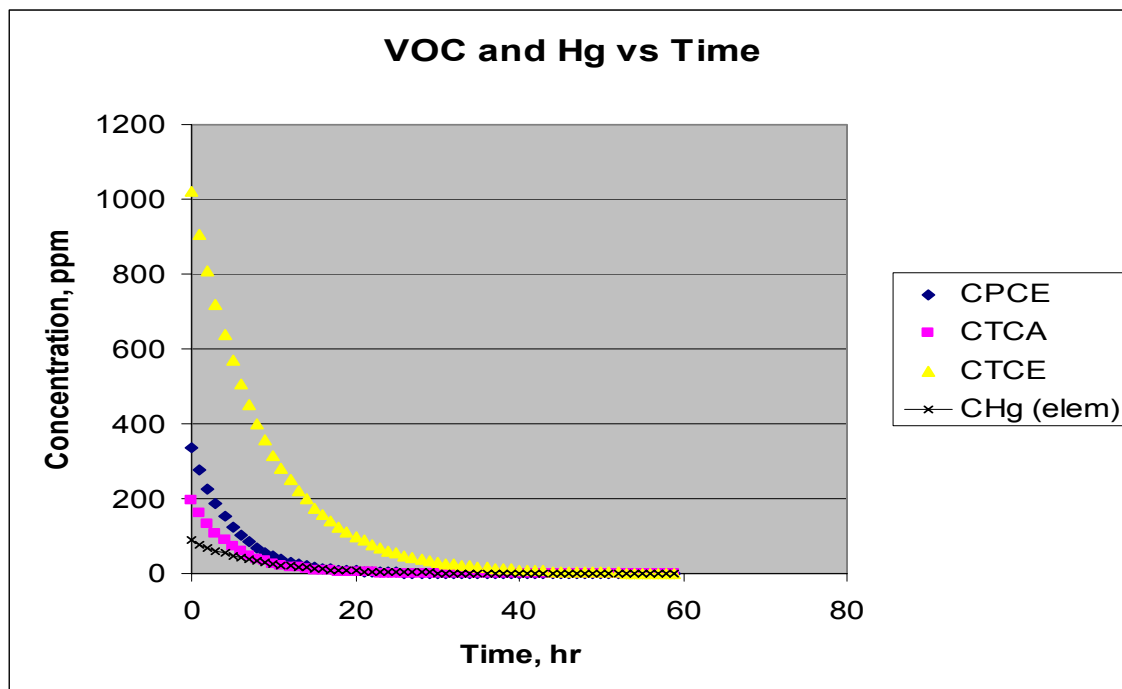
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Figure 9. VOC/Hg vs Time.

4.5   System Sizing and Design

Calculations to determine the total mass of GAC and KI-GAC needed for the remedial action were made by INEEL and separately by the GAC bed vendor (Flanders Filters). The INEEL calculations are shown in Appendix A. The AEA Fenton process offgas system was provided by Flanders filters, hence this vendor was contacted by AEA concerning the GAC adsorption system.

4.5.1   INEEL GAC Calculations

According to the INEEL calculations, approximately 570 lb of GAC for VOC control and 12 lb of KI-GAC for Hg control is estimated to sorb the total inventory of VOCs (52 kg, not including any VOCs evolved from SVOC or PCB degradation during the oxidation/reduction process) and Hg in the V-tanks. The SVOCs have insignificant partial pressures during sparging and are not included (see Appendix A). The total amount of GAC and KI-GAC for both VOC and Hg control is 582lb. Since more GAC is required than KI-GAC, each bed changeout would nominally contain 98% GAC and 2% KI-GAC. At a 65 lb (30 kg) carbon per bed changeout, 9 bed changeouts are estimated during the remedial action. The capacity for the INEEL estimates is 20% for TCA based on the lowest concentration in Table 6.

This estimated capacity is based on the worst-case (for TCA) of the three main VOCs – PCE, TCA, and TCE) isotherm available from the vendor.

Preliminary sizing is done to compare to the vendor numbers as a cross-check (i.e., order of magnitude). The details are included in Appendix A. This sizing (based on these calculations) is preliminary only and is based on removing the entire VOC inventory using a conservative design procedure as described in Appendix A (Army 2001).

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4.5.2   Vendor GAC Calculations

The vendor contracted by AEA has determined an amount of GAC needed for the remedial action based on the results (see Figure 9). They have proposed using KI-GAC only for both VOC and Hg control. In their calculations, they allowed higher VOC and Hg sorption capacities early during sparging, because the higher concentrations provide higher sorption driving forces that result in higher sorption capacities. They have reported that 195 lb of KI-GAC per each consolidation tank will be sufficient to sorb all of the Hg, PCE, TCA, and TCE in the V-Tanks. A total of 390 lb would be necessary for the remedial action. This implies an average VOC sorption capacity of 46%. At 65 lb (30 kg) per carbon bed changeout, 3 changeouts per consolidation tank (6 total for the remedial action) would be necessary. It is suggested that additional units be available for uncertainties, i.e the above capacities may not be realized and more changeouts could occur. Based on the decreasing concentrations, the change-outs per the 42-hour sparge time for each tank are approximately (in elapsed time):

- Changeout 1: After the first 6 hours of the 42-hour sparge time

- Changeout 2: After the next 8 hours of the 42-hour sparge time (14 hours after start of sparging

- Changeout 3: After the next 34 hours of the 42-hour sparge time (42 hours after start of sparging.

4.6   GAC Bed Changeout Frequency Modeling

Modeling was conducted to obtain an order of magnitude estimate of change-out frequency and breakthrough time to compare to vendor estimates. There has been some concern about the length of the MTZand residence times. Therefore, this modeling is also intended to demonstrate that immediate or rapid breakthrough will not occur. The adsorption of VOCs on GAC was modeled using a numerical method and an analytical method discussed in Appendix A. The analytical result is the classical step response when the retardation and inlet concentration are assumed constant. The equation below for the numerical method was solved analytically to obtain the step response for TCA as shown in Figure 10. This shows a steep breakthrough at five hours for TCA alone, a characteristic of true plug flow. The real system will not necessarily match the modeled results but the models provide the appropriate order-of-magnitude comparisons. Both the analytical and the numerical solution indicate that the order of magnitude is correct and that there should be reasonable time before the first GAC unit needs to be replaced.
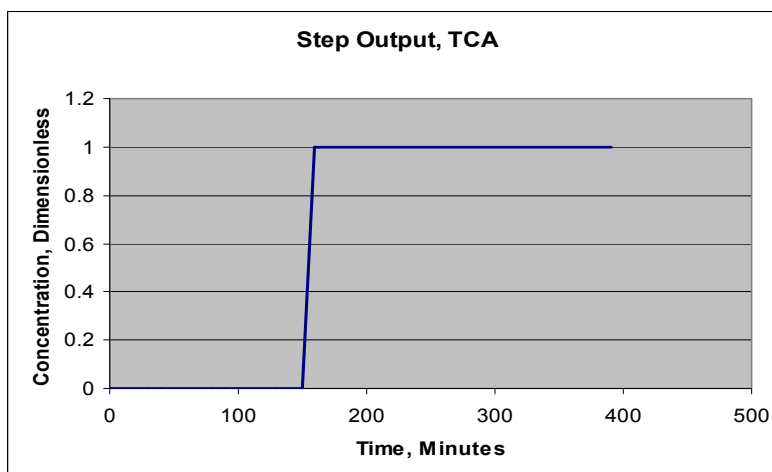

Figure 10. Analytical Result, TCA

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The goal of the numerical method was to provide a predictive model for adsorption of chlorinated organics stripped from V-Tank liquid waste. The target compound modeled was trichloroethylene (TCE). Two separate sets of operating conditions were modeled, as described below.

The mathematical relationships[i] used in the model include a basic material balance:

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} + \frac{1-\varepsilon}{\varepsilon}\frac{\partial q}{\partial t} = 0$$

The solid phase mass transfer relationship is:

$$\frac{\partial q}{\partial t} = k_p a\left(q^* - q\right)$$

An isotherm defines the relationship of q* to the gas phase concentration. For TCE, the isotherm is extremely steep at low gas-phase concentrations then rapidly flattens with increasing TCE concentration. Because of the unusual shape of the isotherm, it was defined mathematically in piecewise fashion in the models. During the initial modeling effort, the relationships for q* were as follows: (a) for gas-phase concentrations below 1.8E-9 moles/ml, q* = 1830436 x c (in moles/ml); (b) above this concentration, q* is considered a constant at 0.00192 moles/ml. In a second modeling effort, the isotherm was defined based on data provided for a different activate carbon product (for Flanders carbon). In this second case, q* = 452452 x c moles/ml up to a gas phase concentration of 3.2E-9 moles/ml and 0.00146 above that point.

To start the modeling process, the code was edited so that program output matched an experimental breakthrough curve published in the open literature (Miyake et al, 2003). This process resulted in an appropriate value of $k_p a$ of 0.6/minute to be used to predict the performance of the full-scale GAC systems with TCE. Specifically, the initial gas-phase concentration was taken as 10,700 ppm$_v$ (4.4E-7 moles/ml), and the flow rate was 210 cfm. The "column" modeled was 2 ft wide, 2 ft long, and 1 foot deep[j]. When the model was applied to these operating conditions using the "calibrated value of $k_p a$, the onset of breakthrough was predicted at about 48 minutes.

In the second modeling effort, the flow rate was increased to 250 cfm, and the maximum TCE concentration in the gas was decreased 1019 ppm$_v$ (4.2E-8 moles/ml). Column dimensions remained the same as in the first model. The second isotherm model described above was also employed. Under these new conditions, the onset of breakthrough occurred at 5 hours and 40 minutes.

In both models, once the mass transfer zone reached the end of the bed, complete breakthrough was very rapid. The breakthrough curves (Figure 10 and Figure 11) are nearly vertical. In Figure 11, once breakthrough begins, the outlet concentration nearly equals the inlet concentration in 8 minutes. In Figure 12, once breakthrough begins, the outlet concentration nearly equals the inlet concentration in 25 minutes. This is consistent with the shapes of the isotherms used.

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i. See Nomenclature.

[j]Note that this model is slightly different as the actual residence time and GAC size is smaller. However, both this and the analytical approach are semi-quantitative and are used for order-of-magnitude analysis for comparison.

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Breakthrough with Co = 10700 ppmv
(Flow = 210 cfm; Qmax = 130 mg/g)

Figure 11. 10700 ppm TCE.

Breakthrough with Co = 1019 ppmv
(Flow = 250 cfm; Qmax = 399 mg/gram)
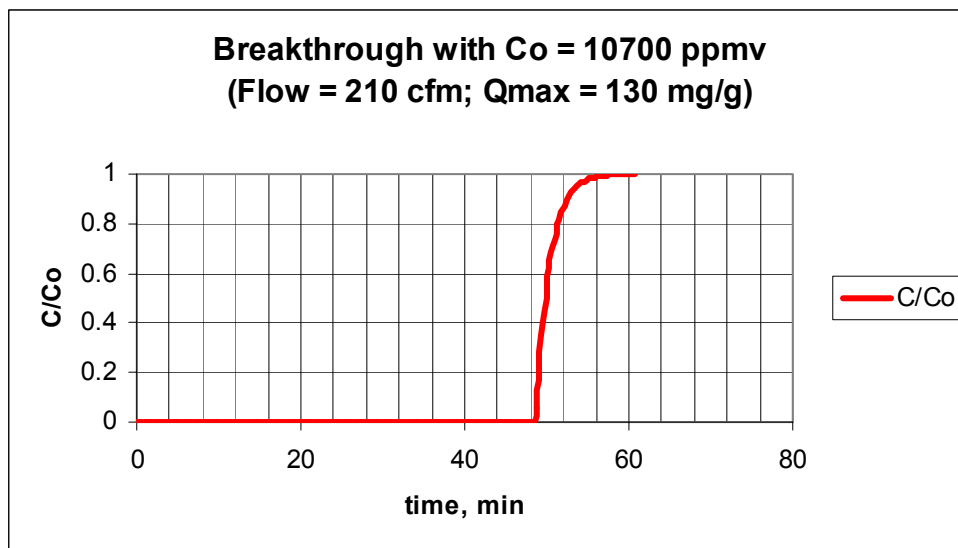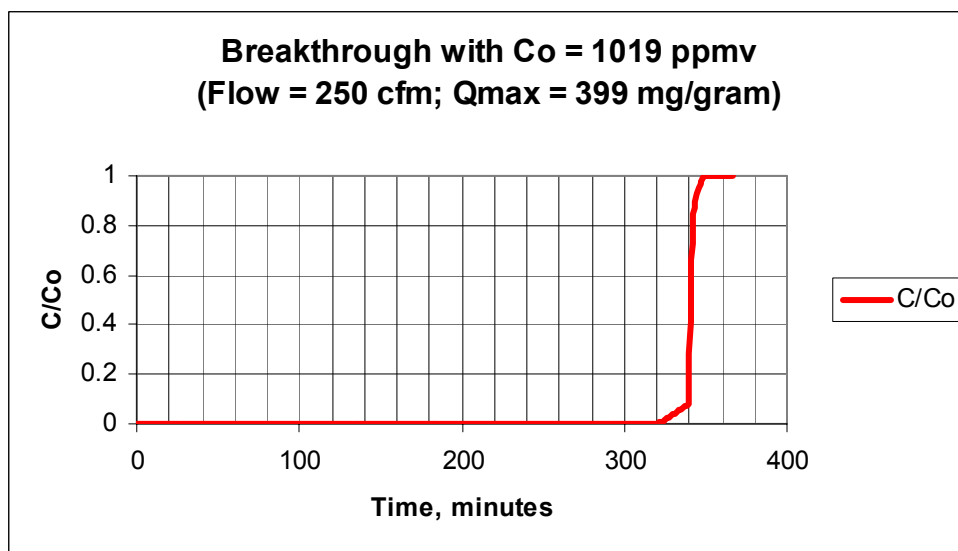
Figure 12. 1019 ppm TCE.

4.7   Potential Radionuclide Depostion on the Activated Carbon

Based on the preliminary sizing, an approximate radionuclide loading was determined. Appendix A provides the details. The loading of radionuclides and metals was estimated by (a) determining the amount of radionuclides that would be entrained with water aerosols and sludge aerosols via entrainment using some data in Perry's 4th ed. (Perry 1963), assuming a particulate and radionuclide decontamination factor (DF) of 10 for the scrubber, , and (b) a DF of 100 for the single HEPA. The loading of radionuclides on the carbon was estimated assuming that all of the radionuclides entrained during sparging, that are not captured by the scrubber or the HEPA, will deposit in the carbon bed. At the low velocities encountered during sparging, there is not much entrainment. However, for radionuclides, it

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does not require a large amount to cause difficulties in waste dispositioning. The estimated radionuclide loadings are provided in Table 7.

Table 7. GAC Loadings From Sparge.

Organics	(mg/kg)	Radionuclides	(Ci/kg)		(Ci/kg)		(Ci/kg)
Bromo methane	2.11E+03	Pu-238	8.84E-14	Co-60	1.42E-12	I-129	4.48E-14
Choloro ethane	8.04E+03	Pu-239/240	2.56E-14	Cs-134	9.06E-14	Ni-63	1.64E-11
Chloro methane	1.34E+03	Am-241	2.26E-14	Cs-137	4.34E-10	H-3	0.00E+00
1,2-dichlorobenzene	6.80E+03	Cm-242	1.37E-15	Eu-152	6.07E-13		
1,3-dichlorobenzene	9.08E+03	Cm-243/244	3.83E-15	Eu-154	2.05E-13		
1,4-dichlorobenzene	9.56E+03	Np-237	5.21E-15	Eu-155	8.00E-13		
1,1-dichloroethane	1.77E+03	U-233/234	1.17E-12	Mn-54	1.48E-13		
1,2-dichloroethylene	3.09E+03	U-235	3.85E-14	Nb-95	4.40E-13		
methylene chloride	8.16E+03	U-238	1.21E-14	Ra-226	2.96E-13		
PCE	9.39E+04	Sr-90	7.29E-10	Ru-103	3.16E-12		
TCA	9.18E+03	Ag-108	2.32E-13	Ru-106	2.73E-12		
1,2,4-trichlorobenzene	5.00E+04	Ag-110	3.97E-13	Sb-125	1.16E-12		
TCE	3.83E+05	Ce-144	2.31E-12	Zn-65	3.29E-13		
Vinyl Chloride	4.00E+03	Co-58	4.03E-13	Zr-95	7.86E-13		
Total Organic, kg	52					Total, Ci	1.1E-07
Metals	mg/kg						
Ba	2.69E-05						
Be	3.14E-06						
Cd	1.99E-06						
Pb	1.06E-05						
Hg	2.98E-06						
Ni	2.31E-05						
Ag	6.98E-07						

5. ESTIMATED STACK GAS VOC, SVOC, AND HG CONCENTRATIONS AND EMISSION RATES

The assumed VOC and Hg removal is based on the efficiencies provided by the vendor, i.e., 99.5% or DF = 200 for mercury that was also assumed for VOCs. At these assumed removal efficiencies, stack gas outlet VOC and Hg concentrations are shown in Table 7 (as the time-weighted average or TWA). The TWA-TLV and other industrial hygiene requirements need to be met for the stripped organics exiting the GAC bed. As shown in Table 8, the TWA-TLV's are easily met without dispersion for PCE, TCA, and TCE at a DF of 200 based on an integral time average. The TWA's were determined from the integral

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average since the concentrations will be a decreasing function of time as shown in Appendix A. The estimated stack gas concentrations are compared to Industrial Hygiene (IH) limits (TWA-TLV, IDLH, etc.) in Table 8. The estimated stack gas concentrations are less than TWA –TLV values except for the Hg species. However, after accounting for reasonable air dispersion that reduces the stack gas Hg concentration by at least 10x for the nearest receptor (a worker standing near the stack) the estimated Hg concentration is lower than the Hg TWA-TLV. An air permit applicability determination (APAD 2003) shows that the remedial action meets the requirements of an air permit exemption, so no air permit is required for the remedial action. The requirements of the air permit exemption are met because, for all VOCs, the stack gas emission rates are less than the IDAPA screening emission limits. Mercury exceeds the APAD values but is still less than the Idaho Applicable Procedures Act (IDAPA) screening limit of 0.001 lb/hr. Based on the APAD (APAD 2003) analysis, the regulatory driver is industrial hygiene (IH), i.e., exposure to the on-site worker. Based on the sparging calculations and TWA estimate for mercury, the IH limit of 0.01 mg/m^3 (NIOSH 2003) would be exceeded (0.03 mg/m^3 for allyl-Hg). Therefore, a separate GAC unit to capture mercury would be required. However, the vendor (Flanders Filters) states that 99.5% of the elemental mercury can be removed using their KI-GAC that is 2 % KI. Using a DF of 200, the mercury still exceeds the TWA-TLV at the discharge. However, dispersion from the 20-ft stack decreases the mercury to below the TWA-TLV for a nearby receptor by about a factor of 2. This is shown in Table 8 and Appendix A.

Table 8. Average Concentrations and Emission Rates.

	Maximum	TWA-TLV[a] (calc)	Emission Rate[a] (lb/hr)	TLV	IDLH	15-minute STEL	Ceiling
PCE	4.7 ppm	2.12 ppm	3.23E-3	25 ppm	150 ppm	100 ppm	200 ppm
TCA	7.68 ppm	3.47 ppm	4.24E-3	10 ppm	100 ppm	N/A	N/A
TCE	22.3 ppm	13.48 ppm	2.03E-2	50 ppm	1000 ppm	N/A	100 ppm
Hg[b] (undispersed)	3.1 mg/m^3	1.58 mg/m^3	5.62E-4	0.01 mg/m^3	2 mg/m^3	0.03 mg/m^3	0.04 ppm
Hg[c] (dispersed)	0.0087 mg/m^3	0.0045 mg/m^3	5.62E-4	0.01 mg/m^3	2 mg/m^3	0.03 mg/m^3	0.04 ppm

a. Calculated based on integral average over 42 hours
b. 0.03 mg/m^3 for allyl Hg, the IDLH for allyl is 10 mg/m^3
c. Based on a 20 ft stack and 6 ft tall worker in stack vicinity

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7. APPENDICES

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Appendix A

GAC Supporting Calculations

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Appendix A, GAC Supporting Calculations

Contents

I. Data. The data below are used in the Estimates

Displacement rate during fill from the V-Tanks to the consolidation tanks:

$$F_d := 50 \frac{gal}{min} \qquad Q_d := F_d \qquad Q_d = 6.68 \frac{ft^3}{min}$$

Pressures and Temperatures

$$P := \frac{12.5}{14.7} atm \qquad T_g := 298K$$

Gas Constants

$$R_g := 0.082 \frac{L \cdot atm}{mol \cdot K} \qquad R_{star} := \frac{R_g \cdot 298K}{P} \qquad R_{star} = 28.737 \frac{L}{mol}$$

Volumes/Masses/Densities

$$V_{tks} := 12000 gal \qquad \text{This is the V-Tank total volume (sludge + liquid)}$$

$$V_{gas} := 2 \cdot 8000 gal - V_{tks} \qquad V_{gas} = 4000 gal \qquad \text{This is the volume of gas in the space above liquid in all tanks combined}$$

$$V_g := \frac{V_{gas}}{2} \qquad \text{Amount of vapor space volume per tank}$$

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$V_{liq} := 10033 \, gal$ This is the volume of liquid (V_{tks} - V_{sludge})

$V_L := \dfrac{V_{liq}}{2}$ This is the liquid volume split into 2 tanks

$V_{tk} := \dfrac{V_{tks}}{2}$ This is the total volume split into 2 tanks

$M_{tk} := \dfrac{7348}{2} \cdot kg$ Sludge Mass per tank

$M := 7348 \, kg$ Total Sludge

$\rho_{GAC} := 500 \dfrac{gm}{L}$ GAC density $\rho_{H2O} := 1 \dfrac{kg}{L}$

Molecular Weights/Henry's Constants/Solid-Liquid Distribution

$MW_{air} := 29 \dfrac{gm}{mol}$ $MW_{dcb} := 147 \dfrac{gm}{mol}$

$MW_{TCE} := 131.4 \dfrac{gm}{mol}$ $MW_{Hg} := 200 \dfrac{gm}{mol}$ $MW_{H2O} := 18 \dfrac{gm}{mol}$

$H_{dcb} := 1.82 \dfrac{L \cdot atm}{mol}$ $H_{PCE} := 16.95 \dfrac{L \cdot atm}{mol}$ $MW_{PCE} := 166 \dfrac{gm}{mol}$

$H_{TCA} := 16.95 \dfrac{L \cdot atm}{mol}$ $H_{TCE} := 10 \dfrac{L \cdot atm}{mol}$ $MW_{TCA} := 133.5 \dfrac{gm}{mol}$

$H_{Aroclor1260} := \dfrac{1}{3.9 \dfrac{mol}{L \cdot atm}}$ $H_{Aroclor1260} = 2.56 \times 10^{-1} \, L \cdot \dfrac{atm}{mol}$

$MW_{Aroclor1260} := (12 \cdot 12 + 5 + 5 \cdot 35.5) \dfrac{gm}{mol}$

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The Henry's coefficient for Hg is (Clever et al 1985):

$$H_{Hg} := \frac{495 atm \cdot MW_{H2O}}{\rho_{H2O}} \qquad\qquad H_{Hg} = 8.91 \frac{L \cdot atm}{mol}$$

Determine the solid - liquid equilibrium constant (Hemond et al 1993)

$$k_D = K_{oc} \cdot f_{oc}$$

(From Hemond et al 1993)

$$\log(K_{oc}) = 0.544 \log(K_{ow}) + 1.377 \qquad\qquad \log(K_{ow}) = 2.5$$

Approximate average for PCE, TCA, and TCE, wide variety

$$K_{oc} := 10^{(0.544 \cdot 2.5 + 1.377)} \frac{mL}{gm} \qquad\qquad K_{oc} = 5.46 \times 10^2 \frac{L}{kg}$$

Determine the f_{oc} from the TOC:

$$TOC := 1.18 \cdot 10^5 \frac{mg}{kg} \qquad\qquad f_{oc} := TOC$$

$$f_{oc} = 1.18 \times 10^{-1}$$

$$k_D := K_{oc} \cdot f_{oc} \qquad\qquad k_D = 6.44 \times 10^1 \frac{L}{kg}$$

For mercury:

$$k_{D\_Hg} := 52 \frac{mL}{gm} \qquad\qquad \text{(http://risk.lsd.ornl.gov/cgi-bin/tox/TOX\_select?select=nrad)}$$

For PCB (using Aroclor 1260)

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$$K_{ow\_Aroclor1260} := 10^{6.5} \frac{L}{kg}$$ (From Hemond et al 1993)

$$K_{oc\_Ar} := 10^{\left(1.00 \cdot \log\left(\frac{K_{ow\_Aroclor1260}}{UnitsOf\left(K_{ow\_Aroclor1260}\right)}\right) - 0.21\right)} \frac{L}{kg}$$ $$K_{oc\_Ar} = 1.95 \times 10^3 \frac{L}{kg}$$

$$k_{D\_Ar} := K_{oc\_Ar} \cdot f_{oc}$$ $$k_{D\_Ar} = 2.3 \times 10^2 \frac{L}{kg}$$

Consolidation Tank

$$D_{imp} := 49 in$$ $$N_{act} := 68 \frac{2 \cdot \pi}{min}$$ $$Q_s := 38 \frac{ft^3}{min}$$ (Sparge)

$$Q_v := 300 \frac{ft^3}{min}$$ V-Tank ventilation

$$D_{tk} := 10 ft$$ $$A_{tk} := \frac{\pi}{4} \cdot D_{tk}^2$$ $$Q_L := 2 \frac{ft^3}{min}$$ (In-Leakage)

$$v_g := \frac{Q_s}{A_{tk}}$$ $$v_g = 2.46 \times 10^{-3} \frac{m}{s}$$ $$P_{ow\_act} := 3.5 hp$$ (EDF-4602)

$$\rho_g := \frac{P \cdot MW_{air}}{R_g \cdot T_g}$$ $$\rho_g = 1.01 \frac{kg}{m^3}$$ $$\rho_L := 1 \frac{kg}{L}$$

Derived Units

$$Ci := 3.7 \cdot 10^{10} s^{-1}$$ Curie definition

Mass Transfer Correlations

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$$b_1 := 0.026 \, W^{-0.4} \cdot m^{0.7} \cdot s^{-0.5}$$ (Perry et al 1984)

$$b_2 := 0.002 \, W^{-0.7} \cdot m^{1.9} \cdot s^{-0.8}$$

The liquid phase mass transfer coefficients are (Perry & Green 1984):

$$k_{La1} = b_1 \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.4} \cdot v_g^{0.5}$$ For pure water/air

$$k_{La2} = b_2 \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.7} \cdot v_g^{0.2}$$ For ionic solutions/air

The P_g is the power reduced as a result of the air around the impeller. It is a function of the impeller diameter and the speed (Treybal 1987).

Let $$\Xi := \frac{Q_s}{N_{act} \cdot D_{imp}^3}$$ $$\Xi = 1.31 \times 10^{-3}$$

Conditional Statement for P_g

$$P_g := \begin{cases} P_{ow\_act} \cdot (0.62 - 1.85\Xi) & \text{if } \Xi > 0.037 \\ P_{ow\_act} \cdot (1 - 12.2\Xi) & \text{otherwise} \end{cases}$$ Note, the P_g is the "gassed" power

$$P_g = 3.44 \, hp$$

$$k_{La1} := b_1 \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.4} \cdot v_g^{0.5}$$ $$k_{La1} = 8.54 \times 10^{-3} \, s^{-1}$$

$$k_{La2} := b_2 \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.7} \cdot v_g^{0.2}$$ $$k_{La2} = 1.65 \times 10^{-2} \, s^{-1}$$

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Although the solid mass transfer is expected to be much higher than $k_L a$, there is still a certain degree of uncertainty. Therefore, use the worst case $k_L a$ of the above 2.

$$k_{La} := k_{La1} \qquad\qquad\qquad k_{La} = 8.54 \times 10^{-3}\, \frac{1}{s}$$

Since this is for air, adjust for TCE related to the diffusivities in water for the two solutes by (Thibodeaux 1979, Crowl et al 1990):

$$\frac{k_{La\_dcb}}{k_{La\_air}} = \left(\frac{D_{dcb}}{D_{air}} \right)^{\frac{2}{3}} \qquad\qquad\qquad \frac{D_{dcb}}{D_{air}} = \sqrt{\frac{MW_{air}}{MW_{dcb}}}$$

$$k_{La\_dcb} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{dcb}} \right)^{\frac{1}{3}} \qquad\qquad\qquad k_{La\_dcb} = 4.973 \times 10^{-3}\, \frac{1}{s}$$

$$k_{La\_PCE} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{PCE}} \right)^{\frac{1}{3}} \qquad\qquad\qquad k_{La\_TCA} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{TCA}} \right)^{\frac{1}{3}}$$

$$k_{La\_Hg} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{Hg}} \right)^{\frac{1}{3}} \qquad\qquad\qquad k_{La\_TCE} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{TCE}} \right)^{\frac{1}{3}}$$

$$k_{La\_Ar} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{Aroclor1260}} \right)^{\frac{1}{3}}$$

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II. Characterization

To determine the applicable VOCs, the data from the characterization report (Tyson 2003) were used. However, these data needed to be filtered. The prescription used was to retain any component that had a detect in any tank in either phase. This was done at the 90% confidence level with the detect values used for the tanks where detect values were listed (i.e., if one tank had an actual number where one or more of the other tanks had detect values, the detect values were averaged together with the actual numbers). This was done at the 90% confidence level using the Microsoft Excel function TINV(probability, degrees of freedom).

$$C_i(90\%) = C_i + \text{TINV}(\Psi, df) \cdot \varepsilon_s$$

For the 2-tailed probability: $\psi = 0.2$

The standard error, ε_s, and the degrees of freedom, df, were taken from the characterization report (Tyson 2003).

Also, there are some miscellaneous effluents that will be added. Most of these will not impact the characterization. The exception is TCA from ARA-16 that is approximately 25,000 mg/kg in the sludge. Therefore, this is weight-averaged into the V-Tank liquids.

Example

Organic Compound. Use 1,3,4 TCB

The following were all at detection limit

$$C_{V1} = C_{V2} = C_{V2} = 1\frac{mg}{L} \qquad\qquad C_{V9} := 0.007$$

$$x_{V1} := 2.01 \cdot 10^{-4}\frac{gm}{gm} \qquad x_{V2} := 1.93 \cdot 10^{-4}\frac{gm}{gm} \qquad x_{V3} := 1.8 \cdot 10^{-4}\frac{gm}{gm}$$

The following for V9 was detectable

$$x_{V9} := 2.9 \cdot 10^{-5}\frac{gm}{gm}$$

According to the algorithm, there was one detect so the totals are based on the detects and non-detects which skews this quite significantly on the conservative side.

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Mass of TCB in liquid at 90% UCL

$M_{V1\_liq} := 0.0112 kg$

$M_{V2\_liq} := 0.011 kg$

$M_{V3\_liq} := 0.0736 kg$

$M_{V9\_liq} := 4.77 \cdot 10^{-6} kg$

Mass of TCB in sludge at 90% UCL

$M_{V1\_sl} := 0.181 kg$

$M_{V2\_sl} := 0.208 kg$

$M_{V3\_sl} := 0.313 kg$

$M_{V9\_sl} := 0.0186 kg$

Total Masses

$M_{liq} := M_{V1\_liq} + M_{V2\_liq} + M_{V3\_liq} + M_{V9\_liq}$

$M_{liq} = 9.58 \times 10^{-2} kg$

$M_{sl} := M_{V1\_sl} + M_{V2\_sl} + M_{V3\_sl} + M_{V9\_sl}$

$M_{sl} = 7.21 \times 10^{-1} kg$

Concentrations

$C_{TCB} := \dfrac{M_{liq}}{V_{liq}}$

$C_{TCB} = 2.52 \dfrac{mg}{L}$

$X_{TCB} := \dfrac{M_{sl}}{M}$

$X_{TCB} = 98.07 \dfrac{mg}{kg}$

$C_{TCB\_tot} := \dfrac{M_{liq} + M_{sl}}{V_{liq}}$

$C_{TCB\_tot} = 2.15 \times 10^{1} \dfrac{mg}{L}$

The next filter consisted of finding the dimensionless form of Henry's Law and comparing it to 0.01 (http://www.cpeo.org/techtree/ttdescript/airstr.htm). If less, then the organic is considered SVOC and not included. For example, all of the phenols were filtered by this process as their H's were less than 0.01. The dimensionless form (H') is found by dividing the L-atm/mol form by RT. Note, this isn't a temperature correction. A temperature correction is given by Sander (Sander 1999).

$$H' = \frac{H(L*atm/mol))}{R(L*atm/mol/°K)*T(298°K)}$$

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The following Table A.1 provides VOC data extracted from the characterization report (Tyson 2003) and recent Henry's Law values along with their equilibrium vapor values (Sander 1999) It is provided as raw data whereas Table A.2 is for calculated distributions after transfer:

Sander used k_H which is 1/H where H is the one used in this EDF and H' is the dimensionless form. The definition for Henry's Law for relating the gas partial pressure of a component to it's liquid phase concentration is:

$$p_i = \frac{1}{k_H} \cdot C_i = H \cdot C_i \qquad\qquad y_i = \frac{p_i}{P} = \frac{H \cdot C_i}{P}$$

Table A.1

	MW	C_i, mg/L	C_i, mol/L	k_H, mol/L/atm	H, L-atm/mol	H'	p_i, atm	y_i, mol fr	y_i, ppm$_v$
Bromo methane	95	0.17	1.74E-06	0.15	6.67	0.27	1.16E-05	1.36E-05	13.62
Choloro ethane	64.5	0.33	5.12E-06	8.50E-02	11.76	0.48	6.02E-05	7.08E-05	70.76
Chloro methane	50.5	0.06	1.12E-06	0.12	8.33	0.34	9.34E-06	1.10E-05	10.97
1,2-dichlorobenzene	147	2.46	1.67E-05	0.55	1.82	0.07	3.04E-05	3.58E-05	35.76
1,3-dichlorobenzene	147.00	2.52	1.72E-05	0.30	3.33	0.14	5.72E-05	6.72E-05	67.21
1,4-dichlorobenzene	147.00	2.52	1.72E-05	0.23	4.35	0.18	7.46E-05	8.77E-05	87.68
1,1-dichloroethane	99	0.10	9.79E-07	0.17	5.88	0.24	5.76E-06	6.77E-06	6.77
1,2-dichloroethylene	97	0.43	4.45E-06	0.13	7.69	0.31	3.43E-05	4.03E-05	40.26
methylene chloride	85	0.61	7.12E-06	0.4	2.50	0.10	1.78E-05	2.09E-05	20.91
PCE	166	0.35	2.11E-06	0.059	16.95	0.69	3.57E-05	4.20E-05	41.97
TCA	133.5	1.30	9.75E-06	0.059	16.95	0.69	1.65E-04	1.94E-04	194.12
1,2,4-trichlorobenzene	181.5	2.52	1.39E-05	0.46	2.17	0.09	3.02E-05	3.55E-05	35.50
TCE	131.5	4.31	3.28E-05	0.1	10.00	0.41	3.28E-04	3.86E-04	385.51
Vinyl Chloride	62.5	0.25	4.02E-06	0.04	25.00	1.02	1.00E-04	1.18E-04	117.95
Mercury (Hg)	200	0.05	2.52E-07	N/A	8.91	0.36	2.25E-06	2.64E-06	2.64

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III. Step 1, Retrieval

Need the composition of the vapors using vapor-liquid-equilibria via Henry's Law. For Henry's Law to be valid, the water mole fraction needs to be near one. This isn't strictly true in this case but the results are believed to be conservative. Also, it is assumed that the equilibria is water-gas and the other phases (e.g., TCE-sludge) do not contribute. This is a typical assumption, i.e., using the top or continuous phase for emission properties (http://www.epa.gov/ttn/chief/faq/tanksfaq.html).

Based on equilibrium, it is assumed that the mass of the individuals above distribute into gas and liquid fractions (i.e., not considering the sludge phase and assuming it remains unchanged). Using a mass basis, the material balance is:

$$M_{tot\_i} = V_{liq} \cdot C_i \qquad\qquad M_i = V_{liq} \cdot C_i = \frac{y_i \cdot V_{gas} \cdot MW_i}{R_{star}} + C_{i\_eq} \cdot V_{liq}$$

$$y_i = \frac{p_i}{P} = \frac{H \cdot C_{i\_eq}}{P}$$

For PCE

$$M_{PCE} := V_{liq} \cdot 0.35 \frac{mg}{L} \qquad\qquad M_{PCE} = 1.33 \times 10^{-2}\, kg$$

$$M_{PCE} = \frac{y_{PCE} \cdot V_{gas} \cdot MW_{PCE}}{R_{star}} + \frac{V_{liq} \cdot y_{PCE} \cdot P \cdot MW_{PCE}}{H_{PCE}}$$

Calculate y_{PCE}

$$y_{PCE} := \frac{M_{PCE}}{\left(\dfrac{V_{gas}}{R_{star}} + \dfrac{V_{liq} \cdot P}{H_{PCE}}\right) \cdot MW_{PCE}} \qquad\qquad y_{PCE} = 3.292 \times 10^{-5}$$

$$y_{PCE\_ppmv} := y_{PCE} \cdot 10^6 \qquad\qquad y_{PCE\_ppmv} = 3.29 \times 10^1$$

$$y_{PCE\_mg} := y_{PCE} \cdot P \cdot \frac{MW_{PCE}}{R_g \cdot T_g} \qquad\qquad y_{PCE\_mg} = 1.9 \times 10^{-1}\, \frac{mg}{L}$$

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$$C_{PCE} := \frac{y_{PCE}P}{H_{PCE}} \cdot MW_{PCE} \qquad\qquad C_{PCE} = 2.74 \times 10^{-1} \frac{mg}{L}$$

Continuing this process for the other VOCs (TCA and PCE, etc.), the following Table A.2 is arrived at where the second column is the mass prior to equilibrium being established between the liquid and gas phases (note various units are provided as vendors may have their data in different units and the gas and liquid concentrations are based on Henry's Law).

Table A.2

	Sludge, kg	Liquid, initial, kg	y_i, MF	y_i, mg/L	y_i, ppmv	C_i, mg/L	Gas, kg	Liq, kg	Total	Total kg
Bromo methane	1.81E-01	6.27E-03	1.23E-05	4.06E-02	1.23E+01	1.49E-01	6.14E-04	5.66E-03	6.27E-03	1.88E-01
Choloro ethane	7.03E-01	1.25E-02	5.94E-05	1.33E-01	5.94E+01	2.77E-01	2.02E-03	1.05E-02	1.25E-02	7.15E-01
Chloro methane	1.17E-01	2.15E-03	9.67E-06	1.70E-02	9.67E+00	4.98E-02	2.57E-04	1.89E-03	2.15E-03	1.19E-01
1,2-dichlorobenzene	5.11E-01	9.34E-02	3.48E-05	1.78E-01	3.48E+01	2.39E+00	2.69E-03	9.07E-02	9.34E-02	6.04E-01
1,3-dichlorobenzene	7.11E-01	9.58E-02	6.38E-05	3.26E-01	6.38E+01	2.39E+00	4.93E-03	9.08E-02	9.58E-02	8.07E-01
1,4-dichlorobenzene	7.54E-01	9.58E-02	8.19E-05	4.19E-01	8.19E+01	2.36E+00	6.34E-03	8.95E-02	9.58E-02	8.50E-01
1,1-dichloroethane	1.54E-01	3.68E-03	6.18E-06	2.13E-02	6.18E+00	8.84E-02	3.22E-04	3.36E-03	3.68E-03	1.58E-01
1,2-dichloroethylene	2.58E-01	1.64E-02	3.58E-05	1.21E-01	3.58E+01	3.84E-01	1.83E-03	1.46E-02	1.64E-02	2.75E-01
methylene chloride	7.03E-01	2.30E-02	2.01E-05	5.94E-02	2.01E+01	5.81E-01	8.99E-04	2.21E-02	2.30E-02	7.26E-01
PCE	8.34E+00	1.33E-02	3.29E-05	1.90E-01	3.29E+01	2.74E-01	2.87E-03	1.04E-02	1.33E-02	8.35E+00
TCA	4.40E+00	4.94E-02	1.52E-04	7.06E-01	1.52E+02	1.02E+00	1.07E-02	3.87E-02	4.94E-02	4.45E+00
1,2,4-trichlorobenzene	7.21E-01	9.58E-02	3.43E-05	2.16E-01	3.43E+01	2.44E+00	3.28E-03	9.25E-02	9.58E-02	8.16E-01
TCE	3.39E+01	1.64E-01	3.32E-04	1.52E+00	3.32E+02	3.71E+00	2.30E-02	1.41E-01	1.64E-01	3.41E+01
Vinyl Chloride	3.46E-01	9.53E-03	8.38E-05	1.82E-01	8.38E+01	1.78E-01	2.76E-03	6.77E-03	9.53E-03	3.56E-01
Mercury (Hg)	4.09E+00	1.92E-03	2.31E-06	1.60E-02	2.31E+00	4.41E-02	2.43E-04	1.67E-03	1.92E-03	4.09E+00
Totals	5.18E+01	6.81E-01					6.24E-02	6.18E-01	6.81E-01	5.25E+01

By material balance and assuming that the V-Tank concentrations and air in-leakage concentrations are zero, the concentrations (mg/L) from Table A.2 are diluted, i.e.:

$$y_{PCE\_dil} := \frac{y_{PCE\_ppmv} \cdot Q_d}{Q_d + 2Q_L + Q_v} \qquad\qquad y_{PCE\_dil} = 7.08 \times 10^{-1}$$

And the rest are calculated similarly and placed in a table in the body of the EDF under step 1.

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IV. Step 2, Sparge the tanks to remove VOCs

Demonstrate that the 3 main VOCs can be removed in 42 hours. Also, determine the time to remove the worst-case VOC, i.e., 1,2 dichlorobenzene (H' = 0.07).

In Appendix B it is shown that the solids-liquid mass transfer coefficient is not rate limiting. Further research indicates that this is the case based on mixer correlations. Therefore, only the liquid-phase transfer coefficient is required. While a more conservative $k_L a$ was used in EDF-4602 Rev.0, additional research has indicated that the correlations are consistent and predict fairly rapid removal.

The transient balance on 1,2-dcb for the solids:

$$\frac{d}{dt} X = -K_{oa\_La}\left(X - \frac{k_D \cdot p}{H} \right) \qquad \text{Since } k_S k_D \gg k_L a \qquad \text{(See Appendix B)}$$

$$K_{oa\_La} := k_{La}$$

Solve for p in terms of X:

$$\omega_S := \frac{Q_S}{R_{star}} \qquad\qquad \omega_S = 0.624 \frac{mol}{s}$$

At any point in time, the mass transfer rate is:

$$\omega = K_{oa\_La} \cdot M \cdot \left(X - \frac{k_D \cdot p}{H} \right)$$

$$\frac{p}{P} = \frac{\omega}{\omega + \omega_S} \qquad\qquad \text{Since } \omega \ll \omega_S \text{ (assumed, this assumption gets worse at lower flow):}$$

$$\frac{p}{P} = \frac{\omega}{\omega_S} = \frac{K_{oa\_La} \cdot M \cdot \left(X - \frac{k_D \cdot p}{H} \right)}{\omega_S}$$

$$p \cdot \left(\frac{1}{P} + \frac{K_{oa\_La} \cdot M \cdot k_D}{\omega_S \cdot H} \right) = \frac{K_{oa\_La} \cdot M \cdot X}{\omega_S}$$

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$$p \cdot \left(\frac{\omega_s \cdot H + K_{oa\_La} \cdot M \cdot k_D \cdot P}{P \cdot \omega_s \cdot H} \right) = \frac{K_{oa\_La} \cdot M \cdot X}{\omega_s}$$

$$p = \Lambda X \qquad\qquad \Lambda := \frac{P \cdot H_{dcb} \cdot k_{La\_dcb} \cdot M_{tk}}{\omega_s \cdot H_{dcb} + k_{La\_dcb} \cdot M_{tk} \cdot k_D \cdot P} \qquad\qquad \Lambda = 0.03 \frac{kg \cdot atm}{mol}$$

Now the derivative can be integrated

$$\int_{X_i}^{X_f} \frac{1}{X} \, dX = -k_{La} \cdot \left(1 - \Lambda \cdot \frac{k_D}{H} \right) t$$

For 99% removal

$$\ln\left(\frac{X_f}{X_i} \right) = -k_{La} \cdot \left(1 - \Lambda \cdot \frac{k_D}{H} \right) t \qquad\qquad t := \frac{\ln(0.01)}{-k_{La\_dcb} \cdot \left(1 - \frac{\Lambda \cdot k_D}{H_{dcb}} \right)} \qquad t = 226.85 hr \quad \text{(For 1,2-DCB)}$$

The above shows that DCB takes longer than the nominal target of 42 hours.

Based on sample extractions during recent sonication testing at MSE, the values for PCE, TCA, and TCA could be off by certain factors (Miller 2004). The error factors applicable to the solid phase resulted based on the difference between known added amounts to the testing surrogate and the baseline analytical results:

$$f_{PCE} := 2.94 \qquad\qquad f_{TCA} := 7.35 \qquad\qquad f_{TCE} := 4.61$$

Check each of these individually to determine if they will be removed by 99% in the sludge phase using the above factors.

$$X_{PCE} := 1140 \frac{mg}{kg} \cdot f_{PCE} \qquad\qquad X_{TCA} := 599 \frac{mg}{kg} \cdot f_{TCA} \qquad\qquad X_{TCE} := 4610 \frac{mg}{kg} \cdot f_{TCE}$$

$$\Lambda_{PCE} := \frac{P \cdot H_{PCE} k_{La\_PCE} M_{tk}}{\omega_s \cdot H_{PCE} + k_{La\_PCE} M_{tk} \cdot k_D \cdot P} \qquad\qquad \Lambda_{PCE} = 0.26 \frac{kg \cdot atm}{mol}$$

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$$t_{PCE} := \frac{\ln(0.01)}{-k_{La\_PCE}\left(1 - \frac{\Lambda_{PCE} k_D}{H_{PCE}}\right)}$$

$$t_{PCE} = 24.6\,hr$$

$$X_{PCE\_f} := 0.001 \cdot X_{PCE}$$

$$X_{PCE\_f} = 3.352\frac{mg}{kg}$$

$$\Lambda_{TCA} := \frac{P \cdot H_{TCA} \cdot k_{La\_TCA} \cdot M_{tk}}{\omega_s \cdot H_{TCA} + k_{La\_TCA} \cdot M_{tk} \cdot k_D \cdot P}$$

$$\Lambda_{TCA} = 2.61 \times 10^{-1}\frac{kg \cdot atm}{mol}$$

$$t_{TCA} := \frac{\ln(0.01)}{-k_{La\_TCA} \cdot \left(1 - \frac{\Lambda_{TCA} \cdot k_D}{H_{TCA}}\right)}$$

$$t_{TCA} = 2.46 \times 10^1\,hr$$

$$X_{TCA\_f} := 0.001 \cdot X_{TCA}$$

$$X_{TCA\_f} = 4.403\frac{mg}{kg}$$

$$\Lambda_{TCE} := \frac{P \cdot H_{TCE} k_{La\_TCE} M_{tk}}{\omega_s \cdot H_{TCE} + k_{La\_TCE} M_{tk} \cdot k_D \cdot P}$$

$$\Lambda_{TCE} = 0.15\frac{kg \cdot atm}{mol}$$

$$t_{TCE} := \frac{\ln(0.01)}{-k_{La\_TCE}\left(1 - \frac{\Lambda_{TCE} k_D}{H_{TCE}}\right)}$$

$$t_{TCE} = 4.15 \times 10^1\,hr$$

$$X_{TCE\_f} := 0.001 \cdot X_{TCE}$$

$$X_{TCE\_f} = 21.252\frac{mg}{kg}$$

For mercury

$$X_{Hg} := 556.8\frac{mg}{kg}$$

$$X_{Hg\_m} := \frac{X_{Hg}}{MW_{Hg}}$$

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$$\Lambda_{Hg} := \frac{P \cdot H_{Hg} \cdot k_{La\_Hg} \cdot M_{tk}}{\omega_s \cdot H_{Hg} + k_{La\_Hg} \cdot M_{tk} \cdot k_{D\_Hg} \cdot P} \qquad \Lambda_{Hg} = 0.17 \frac{kg \cdot atm}{mol}$$

$$t_{Hg} := \frac{\ln(0.01)}{-k_{La\_Hg} \cdot \left(1 - \frac{\Lambda_{Hg} \cdot k_{D\_Hg}}{H_{Hg}} \right)} \qquad t_{Hg} = 3.77 \times 10^1 \, hr$$

Therefore, the 42 hour removal is justified. However, there will be some that are not completely removed and some on appearing on the GAC that are not charaterized (e.g., acetone).

Determine the average, 42 hour, average concentrations based on the 52 kg total and total concentrations in the liquid

$$t_s := 42hr \qquad\qquad y_i = \frac{V_L \cdot C_{i\_tot}}{Q_s \cdot t_s}$$

Using PCE again as an example:

$$C_{PCE\_tot} := 220 \frac{mg}{L} \qquad y_{PCE\_s} := \frac{V_L \cdot C_{PCE\_tot}}{Q_s \cdot t_s} \qquad y_{PCE\_s} = 1.54 \times 10^0 \frac{mg}{L}$$

$$y_{PCE\_ppm} := \frac{y_{PCE\_s}}{MW_{PCE}} \cdot R_{star} \cdot 10^6 \qquad\qquad y_{PCE\_ppm} = 2.67 \times 10^2$$

The rest are calculated similarly and put in a table (Table A.3) and in the body of the report under step 2. Table A.3 is an average based on removing 52 kg of VOCs in 42 hours assuming all of the contaminates emit at the same, constant rate.

Demonstrate that SVOCs are insignificant from sparging using Aroclor 1260 (Ar) as an example.

$$\Lambda_{Ar} := \frac{P \cdot H_{Aroclor1260} \cdot k_{La\_Ar} \cdot M_{tk}}{\omega_s \cdot H_{Aroclor1260} + k_{La\_Ar} \cdot M_{tk} \cdot k_{D\_Ar} \cdot P} \qquad \Lambda_{Ar} = 1.11 \times 10^{-3} \frac{kg \cdot atm}{mol}$$

$$X_{Ar} := 144 \frac{mg}{kg \cdot MW_{Aroclor1260}} \qquad p_{Ar} := \Lambda_{Ar} \cdot X_{Ar} \qquad p_{Ar} = 4.91 \times 10^{-7} \, atm$$

Hence, the SVOCs are insignificant

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Table A.3

	Step 1		Step 2	
Flow, scfm	7	309	38	250
Temperature, °C	25	25	25	25
Humidity (RH)	100	100	100	100
VOCs, ppm$_v$	Raw	Dilute	Raw	Dilute
Bromo methane	12	0.27	10	2
Choloro ethane	59	1.29	59	9
Chloro methane	10	0.21	13	2
1,2-dichlorobenzene	35	0.75	22	3
1,3-dichlorobenzene	64	1.38	29	4
1,4-dichlorobenzene	82	1.77	31	5
1,1-dichloroethane	6	0.13	8	1
1,2-dichloroethylene	36	0.77	15	2
methylene chloride	20	0.44	45	7
PCE	33	0.71	267	41
TCA	152	3.29	32	5
1,2,4-trichlorobenzene	34	0.74	130	20
TCE	332	7.18	1376	209
Vinyl Chloride	84	1.81	30	5
Mercury	2	0.05	109	17

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V. Preliminary Design

A conservative design is to determine the worst-case isotherm (available) and design using the total mass (Army 2001) and compare to vendor estimates. Of the 3 main VOCs, TCA is the worst-case isotherm based on having the lowest Q_{max}. This part is included to compare to the vendor calculations.

The data for TCA is vectorized from the Flanders data in Table A.4 and plotted in Figure A.1. The powerfit (standard Mathcad curve fit routine) values are plotted in Figure A.2:

Table A.4

From Flanders For TCA	
C_{TCA}, ppm	q_{TCA}, g/100g
195	32
108	30
60	27
18	23
2	20

$$q_{TCA}(y) := \begin{pmatrix} 20 \\ 23 \\ 27 \\ 30 \\ 32 \end{pmatrix} \qquad y := \begin{pmatrix} 2 \\ 18 \\ 60 \\ 108 \\ 195 \end{pmatrix}$$

y is ppm per Table A.4

Figure A.1
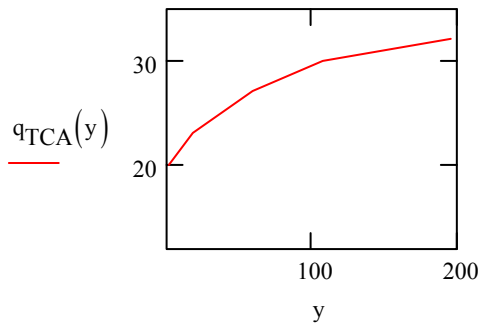
Assume Powerfit $\qquad f(x) = ax^b + c$

guessed vector for constants $\qquad\qquad$ Range $\qquad\qquad\qquad\qquad$ Domain

$$vg := \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \qquad vx := \begin{pmatrix} 0 \\ 2 \\ 18 \\ 60 \\ 108 \\ 195 \end{pmatrix} \qquad vy := \begin{pmatrix} 0 \\ 20 \\ 23 \\ 27 \\ 30 \\ 32 \end{pmatrix}$$

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$$\text{pwrfit}(vx, vy, vg) = \begin{pmatrix} 1.76 \times 10^{1} \\ 1.1 \times 10^{-1} \\ 4.91 \times 10^{-2} \end{pmatrix} \qquad q_{pwr}(y) := 17.6 y^{0.11} + .0491$$

Set the range to plot the domain to

$y := 0, 10 .. 200$

Figure A.2 shows the smoothed function

Figure A.2
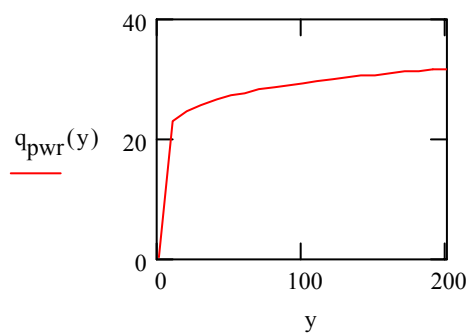
$y_{TCA\_ppm} := 3.29$ (From Table A.3)

$q_{pwr}(y_{TCA\_ppm}) = 2.01 \times 10^{1}$

The mass comes from Table A.2, 52 kg total or 26 kg/tank.

$$M_{GAC\_est} := \frac{52 kg}{q_{pwr}(y_{TCA\_ppm}) \, 0.98} \cdot 100 \qquad M_{GAC\_est} = 581.63 \, lb$$

The KI-GAC at 2% is:

$KI := M_{GAC\_est} \cdot 0.02$ $KI = 1.16 \times 10^{1} \, lb$

The regular GAC is

$GAC_{reg} := M_{GAC\_est} \cdot 0.98$ $GAC_{reg} = 569.996 \, lb$

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A quick estimate of changeout frequency is based on the total size vs the size of the unit, i.e.:

$$M_{unit} := 65 lb$$

$$n := \frac{M_{GAC\_est}}{M_{unit}}$$

$n = 8.95$ so there are 9 changeouts over 84 hours for comparison to vendor's 6 which is expected as this method is conservative

Then the frequency is:

$$freq := \frac{n}{2t_s}$$

$freq = 3\,day^{-1}$ (Note that change-outs are not evenly spaced over the 42-hr period)

Also note that this is the amount needed at saturation, i.e., the gas concentration exiting the GAC columns would be equal to the feed concentration if this GAC loading is desired. In practice, it is necessary to have more GAC to treat the VOCs if the gas-phase concentration is to be kept very low.

The vendor provided a sizing and changeout frequency based on their data for the main VOCs and mercury. This value is 3, 65 lb units per sparge tank so the preliminary estimate is close to the vendor estimates and is an over-design as expected.

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VI. GAC Modeling

This section provides modeling of loading the GAC to help determine changeout frequency, length of mass transfer zone, etc. The model is modified from a liquid ion exchange system (Kimmitt 2004) that used difference equations to model adsorption. This numerical model and results are presented in the body of the EDF. The analytical solution is given below.

Use the isotherm relation for TCA:

The isotherm data from Flanders is shown in Table A.5:

Table A.5

From Flanders For TCA					
C_{TCA}, ppm	q_{TCA}, g/100g	C_{TCA}, g/L	q, g/kg	$J = C/C_{max}$	$Q=q/q_{max}$
2	20	9.14E-06	200	0.01025641	0.625
18	23	8.22E-05	230	0.09230769	0.71875
60	27	2.74E-04	270	0.30769231	0.84375
108	30	4.93E-04	300	0.55384615	0.9375
195	32	8.91E-04	320	1	1

guessed vector for constants   Range   Domain

$$vg := \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \qquad vx := \begin{pmatrix} 0 \\ 0.0103 \\ 0.0923 \\ 0.308 \\ 0.554 \\ 1 \end{pmatrix} \qquad vy := \begin{pmatrix} 0 \\ 0.625 \\ 0.719 \\ 0.844 \\ 0.938 \\ 1 \end{pmatrix}$$

$$pwrfit(vx, vy, vg) = \begin{pmatrix} 9.83 \times 10^{-1} \\ 1.1 \times 10^{-1} \\ 1.52 \times 10^{-3} \end{pmatrix} \qquad Q_{pwr}(J) := 0.983 J^{0.11} + .0015\hat{z}$$

$$corr\left(\overrightarrow{Q_{pwr}(vx)}, vy \right) = 9.98 \times 10^{-1} \qquad \text{An outstanding } R^2$$

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The data was also fitted to a power isotherm using EXCEL and the table values above, i.e.:

a = 0.9755   b = 0.1043   So both methods provide approximately the same answer

Using the MathCad fit: $a := 0.983$ $b := 0.11$ $c := 0.00152$

$$q = a \cdot q_{max} \left[\left(\frac{C}{C_{max}} \right)^b + c \right]$$

The slope is K_D:

$$K_D = \frac{d}{dC} \left[a \cdot q_{max} \left[\left(\frac{C}{C_{max}} \right)^b + c \right] \right] \qquad K_D = a \cdot q_{max} \left(\frac{C}{C_{max}} \right)^b \cdot \frac{b}{C}$$

The numerical model and analytical model use the plug flow differential:

Differential Equation used for plug flow:

$$R \cdot \frac{\partial}{\partial t} C = -v \cdot \frac{\partial}{\partial x} C \qquad\qquad \frac{\partial}{\partial t} C = -\alpha \cdot \frac{\partial}{\partial x} C \qquad\qquad \alpha = \frac{v}{R}$$

Use the Laplace Transform with:

$$C(0,t) = 1 \qquad C(x,0) = 0 \qquad L\left(\frac{\partial}{\partial t} C \right) + \alpha \cdot L\left(\frac{\partial}{\partial x} C \right) = 0$$

$$L\left(\frac{\partial}{\partial t} C \right) = sLC - C(x,0) = s \cdot \Psi \qquad\qquad \alpha \cdot L\left(\frac{\partial}{\partial x} C \right) = \alpha \cdot \frac{d}{dx} \Psi$$

This becomes the ordinary DE:

$$s \cdot \Psi + \alpha \cdot \frac{d}{dx} \Psi = 0$$

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The solution is:

$$\Psi = c(s) \cdot e^{\frac{-s}{\alpha} \cdot x}$$

$$c(s) = L(1) = \frac{1}{s}$$

$$\Psi = \frac{e^{\frac{-s}{\alpha} \cdot x}}{s}$$

The inverse is needed to get $C(x,t)$

$$L^{-1} \left(\frac{e^{\frac{-s}{\alpha} \cdot x}}{s} \right) = \Phi \left(t - \frac{R}{v} \cdot x \right)$$

The inverse can be found by the inversion theorem but it's complicated by the fact that this has a branch point. However, the inverse was found in a table (http://mathworld.wolfram.com/LaplaceTransform.html).

Where Φ is the Heavyside unit function. What this says is that without any retardation, that there is no breakthrough until the residence time elapses. However, due to the retardation from adsorption, it is modified by R. This solution only applies for constant concentration.

$$\rho_B := 0.5 \frac{kg}{L}$$

$$\theta := 0.5$$

The geometry of the GAC is based on a 2' x 2' x 1' box. For a 250 scfm flow, the velocity is based on the box area.

$$Q := 250 \frac{ft^3}{min}$$

$$A_i := 2ft \cdot 2ft$$

$$x := 1ft$$

However, this is the area of the box not the GAC. The vendor says there is a 12 in depth and 65 lb of GAC so the total volume of the box does not contain GAC since the GAC density is 500 g/L. Therefore, the cross-sectional area is:

$$A_i := \frac{M_{unit}}{\rho_{GAC} \cdot x}$$

$$A_i = 2.08 \times 10^0 \, ft^2$$

The superficial velocity is:

v is the actual pore velocity

$$v_s := \frac{Q}{A_i}$$

$$v_s = 2 \times 10^0 \frac{ft}{s}$$

$$v := \frac{v_s}{\theta}$$

The empty bed contact time (EBCT) or superficial residence time is:

$$\tau_{EBCT} := \frac{x}{v_s}$$

$$\tau_{EBCT} = 5 \times 10^{-1} \, s$$

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The worst-case is the starting concentration:

$$C_i := \frac{195}{10^6} \frac{mol}{mol}$$

In terms of mg/L:

$$C_{max} := C_i$$

$$C_{i\_mgL} := \frac{C_i \cdot MW_{TCA}}{R_{star}}$$

$$C_{i\_mgL} = 9.06 \times 10^{-1} \frac{mg}{L}$$

$$q_{max} := 320 \frac{gm}{kg}$$

$$K_D := a \cdot q_{max} \left(\frac{C_i}{C_{max}} \right)^b \cdot \frac{b}{C_{i\_mgL}}$$

$$K_D = 3.82 \times 10^4 \frac{L}{kg}$$

$$R_i := 1 + \frac{\rho_B \cdot K_D}{\theta}$$

$$R_i = 3.82 \times 10^4$$

(The time (t) is varied until Co(t) is non-zero)

$$t := 9600 s$$

$$t = 1.6 \times 10^2 \, mir$$

$$\tau := \frac{x}{v}$$

$$\tau = 2.5 \times 10^{-1} s$$

$$C_o(t) := C_{i\_mgL} \cdot \Phi(t - R_i \cdot \tau)$$

$$C_o(t) = 9.06 \times 10^{-1} \frac{mg}{L}$$

$$t = 2.67 \times 10^0 \, hr$$

Also, the retarded velocity is:
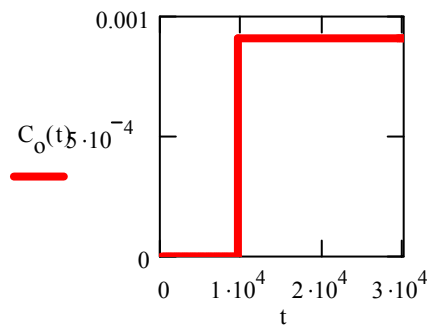
$$v_R := \frac{v}{R_i}$$

$$v_R = 3.19 \times 10^{-5} \frac{m}{s}$$

$$t := 1s, 2s .. 30000 s$$

Figure A.3 shows the plot and the discontinuous step for true plug flow

Figure A.3

This result is simply an indication of the orders of magnitude and validates the vendors claims.

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VII. GAC Loading

In reality, the GAC will also load with particulates. For the organics, the prediction is based on

$$X_i = \frac{C_i \cdot V_L}{M_{GAC}}$$

To find the loadings for radionuclides and metals, an entrainment function is needed. This was determined by plotting the upper curve of C' vs DF in Figure 11-31 of Perry's 4th ed. This provides a particulate entrainment for gas bubbling through a liquid, kg-liq in vapor/kg liquid.

$C_{air} < 120$ $E = 8.3 \cdot 10^{-7} \cdot C_{air}$

$C_{air} > 120$ $E = 10^{-13} \cdot C_{air}^{4}$

Where $C_{air} = \dfrac{G_{air}}{\sqrt{\rho_g \cdot (\rho_L - \rho_g)}}$ $G_{air} := \dfrac{Q_s \cdot \rho_g}{A_{tk}}$

$G_{air} = 1.83 \dfrac{lb}{ft^2 \cdot hr}$ $C_{air} := \dfrac{G_{air}}{\sqrt{\rho_g \cdot (\rho_L - \rho_g)}}$ $C_{air} = 9.227 \times 10^{-1} \dfrac{ft}{hr}$

Since this is less than 120:

$E := 8.3 \cdot 10^{-7} \cdot \dfrac{hr}{ft} \cdot C_{air}$ $E = 7.658 \times 10^{-7} \dfrac{kg}{kg}$ i.e., the gas rate is too low for much entrainment

Applying this to the radionuclides using Sr as an example

$C_{Sr} := 1.24 \, 10^{-5} \dfrac{Ci}{L}$ $y_{Sr} := E \cdot V_L \cdot \dfrac{C_{Sr}}{V_g}$ $y_{Sr} = 2.382 \times 10^{-11} \dfrac{Ci}{L}$ (A gas phase particulate concentration)

The emission rate equals the deposition rate assuming no DF for upstream equipment:

$r_{Sr} := y_{Sr} \cdot Q_s$ $r_{Sr} = 1.54 \times 10^{-6} \dfrac{Ci}{hr}$ $M_{GAC\_vend} := 3.65 lb$

$L_{Sr} := \dfrac{r_{Sr} \cdot t_s}{M_{GAC\_vend}}$ $L_{Sr} = 7.302 \times 10^{-7} \dfrac{Ci}{kg}$ $Q_s = 1.08 \times 10^{3} \dfrac{L}{min}$

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Assuming that there is a DF of 10 from the scrubber and 100 for the HEPA:

$$DF_s := 10 \qquad\qquad DF_H := 100$$

$$L_{Sr2} := \frac{L_{Sr}}{DF_s \cdot DF_H} \qquad\qquad L_{Sr2} = 7.3 \times 10^{-10} \frac{Ci}{kg}$$

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VIII. Site Worker Protection

Mercury was previously targeted for removal. Since the APAD did not identify any problem with mercury, it's based on local worker protection.

Calculate the time weighted average (TWA)-threshold limit vale (TLV) for PCE, TCA, and TCE based on the C vs t relation:

$$p_{o\_PCE} := \frac{\Lambda_{PCE} X_{PCE}}{MW_{PCE}}$$

$$p_{o\_PCE} = 5.26 \times 10^{-3} \, atm$$

Note that these VOCs are based on the factored X's and will not match the plot in the body of the EDF, i.e., they are much higher.

$$p_{o\_TCA} := \frac{\Lambda_{TCA} \cdot X_{TCA}}{MW_{TCA}}$$

$$p_{o\_TCA} = 8.59 \times 10^{-3} \, atm$$

$$p_{o\_TCE} := \frac{\Lambda_{TCE} X_{TCE}}{MW_{TCE}}$$

$$p_{o\_TCE} = 2.5 \times 10^{-2} \, atm$$

$$Q_T := 250 \frac{ft^3}{min}$$

The initial concentrations in ppm_v are:

$$C_{o\_PCE} := \frac{p_{o\_PCE}}{P} \cdot 10^6 \cdot \frac{Q_s}{Q_T}$$

$$C_{o\_TCA} := \frac{p_{o\_TCA}}{P} \cdot 10^6 \cdot \frac{Q_s}{Q_T}$$

$$C_{o\_TCE} := \frac{p_{o\_TCE}}{P} \cdot 10^6 \cdot \frac{Q_s}{Q_T}$$

Note: diluting from 40 scfm to 250 scfm and using the integral average (Chapra et al 1998)

$$mean = \frac{\int_a^b f(x) \, dx}{b - a}$$

$$\Delta t := 10hr$$

$$DF := 200$$

$$\Delta t_e := 42 \cdot hr$$

$$TWA\_PCE := \frac{1}{DF \cdot \Delta t} \cdot \int_0^{10hr} C_{o\_PCE} \cdot e^{\left[-k_{La\_PCE} \left(1 - \frac{\Lambda_{PCE} \cdot k_D}{H_{PCE}} \right) \cdot t \right]} dt$$

$$TWA\_PCE = 2.12$$

Less than the TLV of 25 TWA

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The maximum concentration for mitigated PCE to compare to the IDLH:

$$C_{o\_PCE\_max} := \frac{C_{o\_PCE}}{DF} \qquad\qquad C_{o\_PCE\_max} = 4.7 \times 10^0$$

The emission rate for PCE is:

The emission rate is:
$$\Omega_{PCE} := \frac{MW_{PCE}}{DF \cdot \Delta t_e \cdot R_{star} \cdot 10^6} \cdot \int_0^{42hr} C_{o\_PCE} \cdot Q_T \cdot e^{\left[-k_{La\_PCE} \left(1 - \frac{\Lambda_{PCE} \cdot k_D}{H_{PCE}} \right) \cdot t \right]} dt$$

$$\Omega_{PCE} = 3.23 \times 10^{-3} \frac{lb}{hr}$$

$$TWA\_TCA := \frac{1}{DF \cdot \Delta t} \cdot \int_0^{10hr} C_{o\_TCA} \cdot e^{\left[-k_{La\_TCA} \left(1 - \frac{\Lambda_{TCA} \cdot k_D}{H_{TCA}} \right) \cdot t \right]} dt$$

$$TWA\_TCA = 3.47 \times 10^0 \qquad\qquad \text{Less than the TLV of 10 TWA}$$

The maximum concentration for mitigated TCA to compare to the IDLH:

$$C_{o\_TCA\_max} := \frac{C_{o\_TCA}}{DF} \qquad\qquad C_{o\_TCA\_max} = 7.68 \times 10^0$$

The emission rate for TCA is:

The emission rate is:
$$\Omega_{TCA} := \frac{MW_{TCA}}{DF \cdot \Delta t_e \cdot R_{star} \cdot 10^6} \cdot \int_0^{42hr} C_{o\_TCA} \cdot Q_T \cdot e^{\left[-k_{La\_TCA} \left(1 - \frac{\Lambda_{TCA} \cdot k_D}{H_{TCA}} \right) \cdot t \right]} dt$$

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$$\Omega_{TCA} = 4.24 \times 10^{-3} \frac{lb}{hr}$$

$$TWA\_TCE := \frac{1}{DF \cdot \Delta t} \cdot \int_0^{10hr} C_{o\_TCE} \cdot e^{\left[-k_{La\_TCE} \left(1 - \frac{\Lambda_{TCE} \cdot k_D}{H_{TCE}} \right) \cdot t \right]} dt$$

$$TWA\_TCE = 13.48 \qquad\qquad \text{Less than the TLV of 25 TWA}$$

The maximum concentration for mitigated TCE to compare to the IDLH:

$$C_{o\_TCE\_max} := \frac{C_{o\_TCE}}{DF} \qquad\qquad C_{o\_TCE\_max} = 2.23 \times 10^1$$

The emission rate for TCE is:

The emission rate is:
$$\Omega_{TCE} := \frac{MW_{TCE}}{DF \cdot \Delta t_e \cdot R_{star} \cdot 10^6} \cdot \int_0^{42hr} C_{o\_TCE} \cdot Q_T \cdot e^{\left[-k_{La\_TCE} \left(1 - \frac{\Lambda_{TCE} \cdot k_D}{H_{TCE}} \right) \cdot t \right]} dt$$

$$\Omega_{TCE} = 2.03 \times 10^{-2} \frac{lb}{hr}$$

Mercury

$$k_{La\_Hg} = 4.49 \times 10^{-3} \frac{1}{s} \qquad\qquad \Lambda_{Hg} := \frac{P \cdot H_{Hg} \cdot k_{La\_Hg} \cdot M_{tk}}{\omega_s \cdot H_{Hg} + k_{La\_Hg} \cdot M_{tk} \cdot k_{D\_Hg} \cdot P}$$

$$\Lambda_{Hg} = 1.7 \times 10^{-1} \frac{kg \cdot atm}{mol}$$

$$p_{Hg} := X_{Hg\_m} \cdot \Lambda_{Hg} \qquad\qquad p_{Hg} = 4.73 \times 10^{-4} atm$$

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$$C_{o\_Hg} := \frac{p_{Hg}}{R_g \cdot T_g} \cdot MW_{Hg} \cdot \frac{40}{250} \qquad\qquad C_{o\_Hg} = 6.2 \times 10^2 \frac{mg}{m^3}$$

$$TWA\_Hg := \frac{1}{\Delta t \cdot DF} \cdot \int_0^{8hr} C_{o\_Hg} \cdot e^{\left[-k_{La\_Hg} \left(1 - \frac{\Lambda_{Hg} \cdot k_{D\_Hg}}{H_{Hg}} \right) \cdot t \right]} dt \qquad\qquad TWA\_Hg = 1.58 \times 10^0 \frac{mg}{m^3}$$

The maximum concentration for mitigated Hg to compare to the IDLH:

$$C_{o\_Hg\_max} := \frac{C_{o\_Hg}}{DF} \qquad\qquad C_{o\_Hg\_max} = 3.1 \times 10^0 \frac{mg}{m^3}$$

The emission rate for Hg is:

The emission rate is:

$$\Omega_{Hg} := \frac{1}{DF \cdot \Delta t_e} \cdot \int_0^{42 \cdot hr} C_{o\_Hg} \cdot Q_T \cdot e^{\left[-k_{La\_Hg} \left(1 - \frac{\Lambda_{Hg} \cdot k_{D\_Hg}}{H_{Hg}} \right) \cdot t \right]} dt$$

$$\Omega_{Hg} = 5.62 \times 10^{-4} \frac{lb}{hr}$$

This exceeds the 10-hr TWA of 0.01 mg/m^3 for elemental and 0.03 mg/m^3 for allyl-Hg so check dispersion from a 20 ft stack.

See Figure A.5 for coordinates (the nomenclature of Parnell et al is used). Since the origin is set at the stack centerline, x_{source} and y_{source} are zero. Also, the y is at midplane and also zero.

The concentration at point (x,y,z) is (Parnell et al 2003):

$$C(x,y,z) = \frac{E}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \cdot e^{\frac{-1}{2} \cdot \frac{y^2}{\sigma_y^2}} \cdot \left[e^{\left[\frac{-1}{2} \cdot \frac{(z-H)^2}{\sigma_z^2} \right]} + e^{\left[\frac{-1}{2} \cdot \frac{(z+H)^2}{\sigma_z^2} \right]} \right]$$

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$E := TWA\_Hg \cdot Q_T$

$u := 15 \dfrac{mi}{hr}$

$z := 6ft$

$H_s := 20ft$

$y := 0ft$

$\theta := 45deg$

Note, z is the height of an individual

$x_{rec} := 5ft$

$x_{source} := 0ft$

$y_{rec} := 5ft$

$y_{source} := 0ft$

$X := (x_{rec} - x_{source}) \cdot \sin(\theta) + (y_{rec} - y_{source}) \cdot \cos(\theta)$

$X = 2.16 \times 10^0 \, m$

Figure A.4
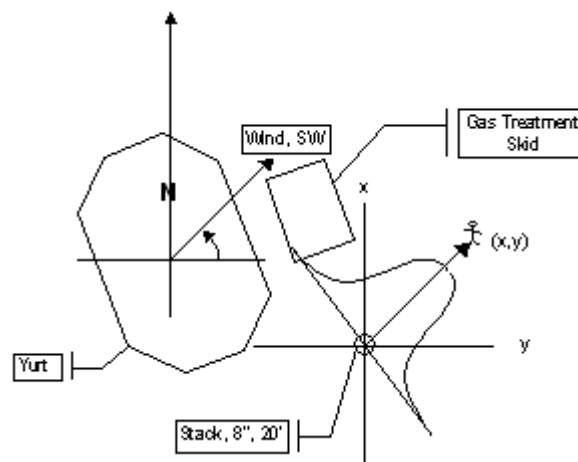
Worst-case is Class F. For less than 0.2 km,

$a := 15.209m$

$b := 0.81558$

$c := 4.1667deg$

$d := 0.36191deg$

$T_i := c - d \cdot \ln\left(\dfrac{X}{UnitsOf(X)}\right)$

$T_i = 3.89 \times 10^0 \, deg$

$\sigma_y := \dfrac{X \cdot \tan(T_i)}{2.15}$

$\sigma_z := a \cdot \left(\dfrac{X}{UnitsOf(X)}\right)^b$

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$$\sigma_y = 6.81 \times 10^{-2}\,m \qquad\qquad\qquad \sigma_z = 2.85 \times 10^{1}\,m$$

$$C_{Hg} := \frac{E}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \cdot \left[e^{\left[\frac{-1}{2} \cdot \frac{y^2}{\sigma_y^2} \right]} \cdot \left[\left[e^{\left[\frac{-1}{2} \cdot \frac{(z-H_s)^2}{\sigma_z^2} \right]} \right] + e^{\left[\frac{-1}{2} \cdot \frac{(z+H_s)^2}{\sigma_z^2} \right]} \right] \right]$$

$$C_{Hg} = 0.00446\,\frac{mg}{m^3}$$

Thus meeting the TWA-TLV by about a factor of 2 for elemental and allyl-Hg at the worst-case position of (5 ft, 5 ft, and 6 ft tall individual) in-line with the prevailing SW winds.

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Nomenclature

a,b,c,d	Constants, various
A	Area
C	Concentration
C_{air}	Virtual air velocity
D	Diameter
df	Degrees of Freedom
DF	Decontamination factor
D_{imp}	Impeller diameter
D_{tk}	Tank diameter
E	Entrainment, emission rate
F_d	Displacement liquid flow
fi	Error factors for VOCs
f_{oc}	Fraction organic carbon
g_c	Gravity conversion
g	Gravity acceleration
G	Mass velocity
h	Height
H	Henry's constant, stack height
H'	Dimensionless Henry's constant
J	Dimensionless concentration
k_D	Solid-liquid partition coefficient
K_D	Gas-GAC partition coefficient
k_H	Inverse Henry's (i.e. solubility)
$k_L a$	Liquid phase mass transfer coefficient
$K_{oaL}a$	Overall mass transfer coefficient
K_{oc}	Organic carbon partition coefficient
K_{ow}	Octanol-water partition coefficient
L	Loading, Laplace transform
L^{-1}	Inverse Laplace transform
m	Moles
M	Mass
MW	Molecular Weight
n	Number of something
N	Impeller speed
ΔP	Pressure drop
p_i	Partial pressure of i
P	Pressure
P_{ow}	Power
q	Isotherm, mL/g
Q	Flow rate, Dimensionless q
Q_d	Displacement gas flow
Q_L	Gas leak flow
Q_s	Sparge gas flow

Q_T	Total gas flow
Q_v	V-Tank Vent flow
r	Rate
R	Retardation factor
R^2	Correlation coefficient
R_g	Gas constant
R_{star}	Volume per mole
t	Time
T	Temperature, 1/2 Pasquill Θ
TINV()	EXCEL worksheet function
u	Wind velocity
v	Velocity
v_R	Retarded velocity
vg	Guess vector
vx	x data vector
vy	y data vector
V	Volume
y_i	ppm or Mole fraction of i, gas

Greek

α	v/R
ε_S	Efficiency
θ	Porosity
Θ	Wind angle
Λ	Stripping factor
ρ	Density
σ_y	Horizontal dispersion
σ_z	Vertical dispersion
τ	Residence time
Ξ	Gassed power number
Φ	Heavyside step function
Ψ	Probability, transformed variable
ω	Mole rate, mass transfer
Ω	Emission rate

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Appendix B

Air Stripping of VOCs for Slurries in a Batch Air-Sparged, Agitated Tank

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Appendix B

Air Stripping of VOCs from Slurries in a Batch Air-Sparged, Agitated Tank

1. BACKGROUND

Chlorides represent a potential materials corrosion problem for treating V-Tank wastes. If chlorinated VOCs are stripped out prior to any treatment (for PCB, BHP, etc.), the residual chloride level is reduced to 100-200 mg/L. This document attempts to explain some of the complicating factors associated with stripping, provide justification for testing methodology, and to provide initial estimates for laboratory conditions. Further, it discusses the methods of obtaining required mass transfer coefficients for scale-up to apply to the full-scale system.

2. INTRODUCTION

Figure B-1 shows a transfer from mole fraction x_A in the bulk liquid to an interface at x_{Ai}. Figure B-2 illustrates the driving force concepts. This is called the liquid phase transfer and is designated as:

$$N_{AL} = k_L^{'}(x_A - x_{Ai}) \tag{1}$$

At the interface, the liquid and gas are in equilibrium such that:

$$y_{Ai} = H^{'}x_{Ai} \tag{2}$$

The transfer continues as long is there is a driving force[k] from y_{Ai} to y_A. If the rates are low[l] (Thibodeaux 1979), then the gas transfer is designated as:

$$N_{AG} = k_G^{'}(y_{Ai} - y_A) \quad (3)$$

These two rates are equal and designated N_A. There are two overall relations that can be used interchangeably depending on the ease of use. These are based on virtual or non-existent liquid concentration in the vapor ($x_A^* = y_A/H$) and vapor concentration in the liquid ($y_A^* = x_AH$)[m]:

$$N_A = K_L^{'}(x_A - x_A^*) \tag{4}$$

$$N_A = K_G^{'}(y_A^* - y_A) \tag{5}$$

Adding the differences, $K_L^{'}$ is found, hence:

---

[k]. If there is no driving force, the curves are flat and the gas is in equilibrium with the liquid.

[l]. Otherwise, the mass transfer coefficient may be a function of the mass transfer rate.

[m]. Note that although these are virtual, they are used extensively in mass transfer.

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$$\frac{N_A}{K_L^{'}} = \left(x_A - x_{Ai}\right) + \left(x_{Ai} - x_A^{*}\right)$$

(6)

Since $y_{Ai} = H'x_{Ai}$ and $y_A = H'x_A^{*}$ and canceling the NA's:

$$\frac{1}{K_L^{'}} = \frac{1}{k_L^{'}} + \frac{1}{H^{'}k_G^{'}}$$

(7)

A similar derivation can be done for the gas phase with the result being:

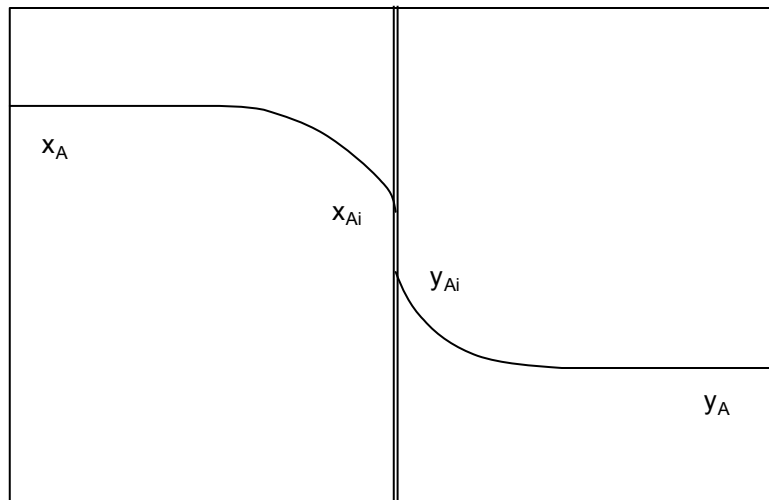$$\frac{1}{K_G^{'}} = \frac{1}{k_G^{'}} + \frac{H^{'}}{k_L^{'}}$$

(8)

Figure B-1. Interphase Mass Transfer, Stripping.

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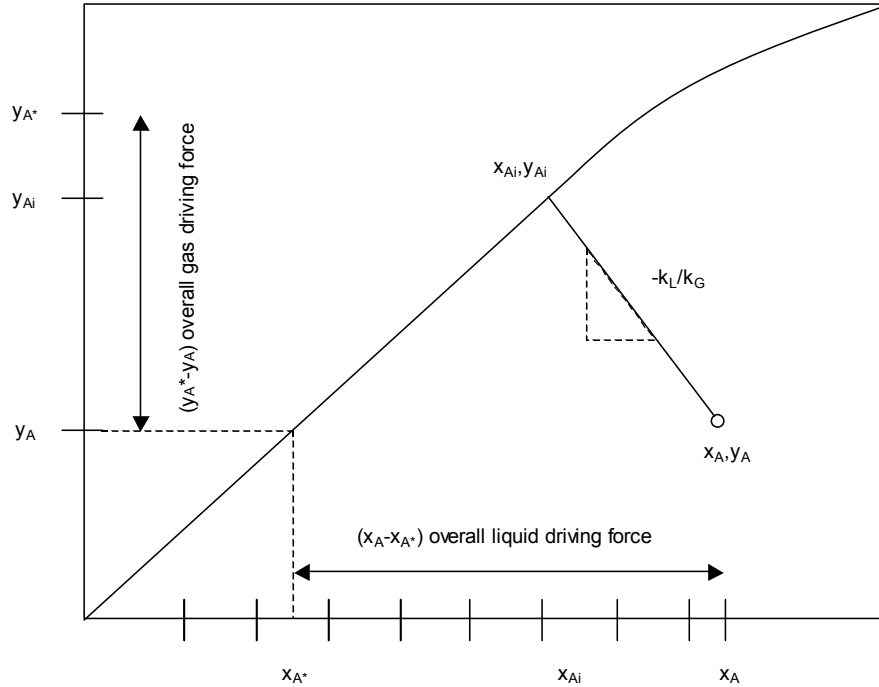
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Figure B-2. Interphase Driving Forces.

An analogue can be found using concentrations with appropriate Henry's Law constants and mass transfer coefficients, i.e.:

$$N_A = K_L (C_A - C_A^*) \tag{9}$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \tag{10}$$

For VOC's, the liquid phase is normally controlling[n]. Further, the areas needed for an actual molar flow rate are difficult to determine and are usually lumped together.

$$K_L \cong k_L \tag{11}$$

$$k_L A = k_L a V \tag{12}$$

Where the "a" is the specific area of bubbles per volume of batch tank.

An analogous method is performed for the solid to liquid transfer as shown in Figure B-3.

$$N_{AS} = k_S \left(X_A - X_{Ai} \right) \tag{13}$$

$$N_{AL} = k_L \left(C_{Ai}^s - C_{Ai}^L \right) \tag{14}$$

---

[n]. Note, some use K_L and k_L interchangeably.

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$$N_{AG} = k_G (p_i - p) \tag{15}$$

$$N_A = K_{oaS}(X_A - X_A^{**}) \tag{16}$$

$$N_A = K_{oaL}(C_A^{**} - C_A^{*}) \tag{17}$$

Where $C_A^{**} = X_A/k_D$, with k_D being the distribution coefficient. A relation is needed for the **'s. The X_A^{**} needs to be is mol/kg or mg/kg so that:

$$X_A^{**} = \frac{p_A k_D}{H} \tag{18}$$

Likewise with C_A^{*}:

$$C_A^{*} = \frac{p_A}{H} \tag{19}$$

The method of finding the overall coefficient based by necessity on the liquid coefficient is:

$$\frac{N_A}{K_{oaL}} = \left(C_A^{**} - C_{Ai}^{S}\right) + \left(C_{Ai}^{S} - C_{Ai}^{L}\right) + \left(C_{Ai}^{L} - C_A^{*}\right) \tag{20}$$

$$\frac{N_A}{K_{oaL}} = \frac{1}{k_D}\left(X_A - X_{Ai}\right) + \frac{N_A}{k_L} + \frac{1}{H}(p_i - p) \tag{21}$$

$$\frac{1}{K_{oaL}} = \frac{1}{k_D k_S} + \frac{1}{k_L} + \frac{1}{H k_G} \tag{22}$$

As discussed previously, there is a need for areas to obtain molar or mass rates:

$$\frac{1}{K_{oaL} a_{oa}} = \frac{1}{k_D k_S a'} + \frac{1}{k_L a} + \frac{1}{H k_G a} \tag{23}$$

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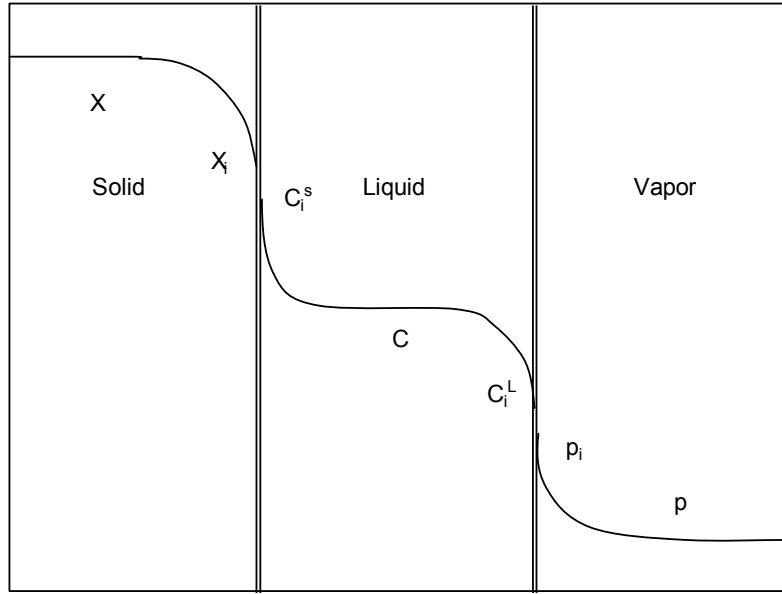
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Figure B-3. Overall Transfer.

3. ESTIMATING RATES FROM CORRELATIONS

Solids-Free Water. For solids-free water and liquid rate limiting, the following is found:

$$\frac{dC}{dt} = k_L a \left(C - C^* \right) \tag{24}$$

Since both quantities vary, need a relation between C and C^*. The instantaneous mass transfer is:

$$\omega = k_L a V \left(C - C^* \right) \tag{25}$$

Since the pressure fraction = volume fraction:

$$\frac{p}{P} = \frac{\omega}{\omega + \omega_{air}} \tag{26}$$

$$\frac{p}{P} = \frac{k_L a V \left(C - C^* \right)}{\omega + \omega_{air}} \tag{27}$$

If it is assumed that $\omega \ll \omega_{air}$, then (27) becomes:

$$\frac{p}{P} = \frac{k_L a V \left(C - p/H \right)}{\omega_{air}} \tag{28}$$

$$p = \frac{k_L a V P H C}{H \omega_{air} + k_L a V P} \cong \frac{k_L a V P C}{\omega_{air}} \tag{29}$$

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The above (29) indicates that p is small and p/H (C*) is smaller and can be neglected in (24) for some cases.

If the assumption in (28) cannot be made:

$$p = \frac{-b - \sqrt{b^2 - 4\chi C}}{2\chi} \tag{30}$$

Where $\quad b = -\left(\frac{1}{H} + \frac{C}{P} + \frac{\omega_{air}}{k_L aVP} \right), \quad \chi = \frac{1}{HP}$

The mass transfer coefficient is dependent on the physics of the system and not the concentration or the mass transfer rate at low rates. The general correlation has been found to be:

$$k_L a = \alpha \left(\frac{P'}{V_L} \right)^\beta v_G^\gamma \tag{31}$$

The constants α, β, and γ in (31) vary depending on the reference but based on several references (Perry & Green, 1984, Harnby et al 1992), it is recommended that: "α" be found by experiment, β and γ from Harby or Perry's. Without any experimental data, it is recommended that "α" take one of the values for non-ionic liquids for this particular case.

Several other correlations were found that indicate the kLa from Perry's is applicable, that is if testing on the actual waste cannot be done. The literature includes:

Van't Riet (Nan't Riet 1979) that appears to be the original data quoted by Perry's

Yagi et al 1975

Valentin 1967

Höcker et al 1981

Zlokarnik 1978

Using the calculated $k_L a$, the time is found by integrating (24):

$$t = \frac{-1}{k_L a} \ln\left(\frac{C_f}{C_i} \right) \tag{32}$$

Solids-Containing Water. For the case of solids containing VOCs in addition to the liquid, the overall coefficient needs to be used in terms of the liquid:

$$\frac{dC^{**}}{dt} = K_{oaL} a_{oa} (C^{**} - C^*) \tag{33}$$

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$$\frac{dX/k_D}{dt} = K_{oaL}a_{oa}(X/k_D - \frac{p}{H})$$ (34)

$$\frac{dX}{dt} = K_{oaL}a_{oa}(X - \frac{k_D p}{H})$$ (35)

Where $\quad K_{oaL}a_{oa} = \dfrac{1}{\dfrac{1}{k_D k_S a'} + \dfrac{1}{k_L a}}$

From Chrysikopoulos et al 2003 it is found that K_p levels out at about 0.06 cm/h shown in B-4 (the liquid velocity from mixing in an air-sparge, agitated system past a particle is expected to exceed this). However, it's not an equivalent analogue. Braida (Braida and Ong, 2000) correlated the k_S with the Sherwood number for air flowing through porous particles that may be a better analogue:

$$Sh = \frac{k_S a' d_p^2}{D}$$ (36)

The Sherwood number for like-kind systems is (see Oldshue 1983, Harnby 1992) :

$$Sh = 2 + 0.72 \, Re_p^{1/2} \, Sc^{1/3}$$ (37)

This becomes 2 as $d_p \rightarrow \infty$ so (37) can be set to 2 and obtain:

$$k_S = \frac{2D}{a' d_p^2}$$ (38)

The specific surface area (a') can be calculated based on the mmpd, 144 mμ.

$$a' = \frac{3(1-n)}{2D_p \rho_s} = \frac{3*0.5}{2*144x10^{-6}\rho_s} = \frac{5200 \, m^2/m^3}{1.4kg/L} = 3.7m^2/kg$$ (39)

The time to remove is then entirely analogous to the solids-free water system shown in (32).

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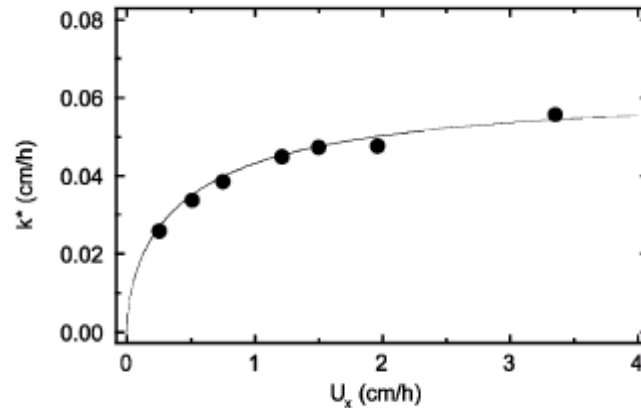01/30/2003
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Figure B-4. Solid mass Transfer Coefficient.

Determine the k_S from (38). The diffusion coefficient for TCE is $D = 9.1x10^{-6}$ cm^2/s.

$$k_S = \frac{2*9.1x10^{-6}\,cm^2/s}{3.7m^2/kg*(0.0144cm)^2} = 2.37x10^{-2}\,kg/m^2/s$$

Using the $k_L a$ from Perry's[o] (Perry & Green 1984)

$$k_L a = 0.026\left(\frac{P_g}{V_L}\right)^{0.4} v^{0.5} = 0.026\left(\frac{.1W}{.001m^3}\right)^{0.4}\left(2.3x10^{-4}\,m/s\right)^{0.5} = 2.5x10^{-3}\,s^{-1}$$

$$K_{oaL}a_{oa} = \frac{1}{\frac{1}{k_D k_S a'} + \frac{1}{k_L a}} = \frac{1}{\frac{1}{64L/kg*2.37x10^{-2}\,kg/m^2/s*10^{-3}\,m^3/L*5200m^2/m^3} + \frac{1}{2.5x10^{-3}\,s^{-1}}} \approx 2.5x10^{-3}\,s^{-1}$$

The above indicates that only the resistance from liquid is needed.

4. LABORATORY ANALYSIS

The best method is to find the constants in (31) for solids-free water. Then, $k_L a$ is known for any condition for this water and can be used for scale-up. The solids-water system coefficient (k_S) would then be found from the overall coefficient. These types of tests would provide a fairly high degree of confidence in the scale-up to the actual system being procured since the correlation is not known for k_S.

If only a single test can be done based on vapor space analysis, a fairly crude but useful K_{oa} can be found. Also, it is recommended to use (31) for the scale-up with "a" determined from the single test and assuming the K_{oa} is correlated by (31). Similar to (26):

---

o. For the assumed laboratory apparatus.

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$$\frac{p}{P} = \frac{K_{oaL}a_{oa}M(X - \frac{k_D p}{H})}{K_{oaL}a_{oa}(X - \frac{k_D p}{H})M + \omega_{air}} \tag{40}$$

The mass transfer is normally much smaller than the molar air rate, $\omega << \omega_{air}$ so that:

$$\frac{p}{P} = \frac{K_{oaL}a_{oa}M(X - \frac{k_D p}{H})}{\omega_{air}} \tag{41}$$

Solving for X:

$$X = p\left(\frac{\omega_{air}}{PK_{oa}a_{oa}M} + \frac{k_D}{H}\right) = \Gamma p \tag{42}$$

Using (34):

$$\frac{dp}{dt} = -K_{oaL}a_{oa}(p - \frac{k_D p}{H\Gamma}) \tag{43}$$

Based on (43), plotting ln(p) versus t will result in a straight line with the following slope:

$$Slope = -K_{oa}a_{oa}\left(1 - \frac{k_D}{H\Gamma}\right) \tag{44}$$

It may be that $H\Gamma >> k_D$ so that this last term can be dropped within the experimental error bounds. The stripping depends on Henry's Law constant as shown in (38). If $k_D/H\Gamma \geq 1$, then no stripping occurs and the air flow is increased to obtain stripping.

$$p = p_o e^{-K_{oaL}a_{oa}(1 - \frac{k_D}{H\Gamma})t} \tag{45}$$

If the assumption in (41) cannot be made, a complicated polynomial function results that will require evaluation.

5. NOMENCLATURE

a	Bubble specific surface area, m^2/m^3
a'	Particle specific surface area, m^2/m^3
a_{oaL}	Overall specific surface area, m^2/m^3
C	Concentration, mol/L
C^*	Non-existent liquid concentration in vapor, mol/L
C^{**}	Non-existent liquid concentration in solid, mol/L

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D	Molecular diffusion, cm^2/s
H	Henry's Law constant, L-atm/mol
H'	Henry's Law constant, mol frac/mol frac
k_D	Solid-liquid distribution coefficient, L/kg
k_G	Individual gas phase coefficient, m/s
k_L	Individual liquid phase coefficient, m/s
$k_L a$	Liquid phase combined coefficient, s^{-1}
$k_G{'}$	Individual gas phase coefficient, mol/m^2-s
$k_L{'}$	Individual liquid phase coefficient, mol/m^2-s
K_G	Overall coefficient based on gas, m/s
K_L	Overall coefficient based on gas, m/s
$K_G{'}$	Overall coefficient based on gas, mol/m^2-s
$K_L{'}$	Overall coefficient based on gas, mol/m^2-s
K_{oa}	Overall mass transfer coefficient, m/s
M	Mass solids, kg
p	Partial pressure, atm
P	Pressure, atm
Re_p	Reynolds number, particle
Sc	Schmidt number
Sh	Sherwood number
V_L	Liquid volume in tank, L
X	Solids concentration, mol/kg
X^*	Non-existent solid concentration in liquid, mol/kg
X^{**}	Non-existent solid concentration in gas, mol/kg
α, β, γ	Scaling constants
Γ	Stripping parameter, solids

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Appendix C

Vendor Information

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VOC Monitoring

ECO SENSORS

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e-mail: sales@ecosensors.com
SANTA FE, NM USA
www.ecosensors.com

Simple, Inexpensive VOC Gas Sensors

MODEL C-12
Visual Display Only • Lowest Cost

MODEL C-21
Includes Audio Alarm, Battery Operation and Provision for External Alarm and Data Logger

FOR PAINT SHOPS, PRINTERS, DRY CLEANERS, WOODWORKERS, VEHICLE REPAIR FACILITIES, CHEMICAL PRODUCTION AREAS AND WHEREVER INDOOR AIR QUALITY MONITORING IS REQUIRED.

The Eco Sensors® Model C-12 and C-21 gas sensors *help* you comply with the new VOC air quality regulations for hydrocarbon gases and solvent vapors.

BENEFITS

— Constantly monitors your work environment. Detects leaks and poor air quality before they are a health hazard. Alarms below OSHA TLV for most common solvent-based VOCs.

— No installation. Easily used and understood by non-technical personnel.

— Virtually no maintenance.

FEATURES

• Highly sensitive to solvent vapors and other VOCs. Bright green-yellow-red display clearly shows hazard level of gas or vapor. Model C-21 also features audio alarm and data logging connection.

• Detects down to OSHA, EPA, and other regulatory-mandated levels…typically at low ppm concentrations.

• Has built-in rechargeable battery for portable use in tracking leaks.

• Rugged construction with many safety features.

SPECIFICATIONS

Range: Full scale = 50-100 ppm for most solvent based VOCs.
Bargraph Display: Green = normal. Yellow = caution. Red = danger
Response time: Within a few seconds of the VOC gas reaching the sensor.
Measurement Principle: HMOS (heated metal oxide semiconductor) sensor.
Size: 85 X 35 X 60 mm (3 1/4" X 1 3/8" X 2 3/8").
Weight: 140 grams (5 oz.).
Power Requirements: 12 volts DC at 300 mA. AC adapters available worldwide.
Battery: Self-contained NiCad or NiMH. Approximately 2 hour capacity. Recharged by AC adapter overnight.

AVAILABLE FROM LEADING DISTRIBUTORS AND OEMs

ECO SENSORS… INNOVATION IN
LOW COST ENVIRONMENTAL MONITORING EQUIPMENT

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ECO SENSORS, INC.

VOC GAS SENSOR
Model C-21

INSTRUCTIONS FOR USE

GENERAL

The model C-21 is a solid-state gas monitor capable of sensing a variety of gases and vapors. The ones it is generally sensitive to are called VOCS (volatile organic compounds), and the most common application of the C-21 is for solvent vapors. Common examples are paint thinners, dry cleaning fluids, cleaning solvents, and gasoline vapors. The instrument does not respond to carbon dioxide or radon, and has only a weak response to carbon monoxide. The C-21 is self-contained except for its AC adapter power module. The instrument also has an audio alarm and has outputs to external alarms, data loggers, calibration equipment, etc.

OPERATION

Plug the AC adapter into AC power and plug the adapter's output plug into the power jack on the instrument. After a few seconds, most or all of the display will light up; it will stay high for 1-2 minutes; and then it will go down to as low as one green bar. The C-21 will require at least 3 minutes to warm-up, and 5 or more minutes is recommended.

The alarm will go on while the instrument's display is in the red including during warm-up. If this is too objectionable, you may put a muffling cloth such as a towel over the instrument during warm-up, or you may switch the alarm off through a hole in the back cover (see illustration to the top right).

One green bar lit indicates the instrument is receiving correct power. Illumination to the first yellow bar indicates a cautionary situation for most VOCs, and reaching the first red bar often indicates a hazardous condition such as reaching the OSHA TLV.

Test the instruments response by holding a fresh felt marker pen a few millimeters from the sensor grill for a few seconds. The display should light up to red. Check the C-21's response to gases and solvents of interest by exposing the instrument to these VOC's and noting its response. The C-21's response to common VOC's is shown on the reverse side of this instruction sheet.

It is best for your protection and for the instrument itself to leave it on 24 hours a day.

INSTALLATION

The instrument may be hung on hooks, screws, etc. using the outer two top holes on the back, or it may be stuck to machinery cabinets, etc. using its magnetic backing. Avoid areas that have a lot of vibration, dust, or dripping or sprayed water. The instrument is not designed for outdoor use. For dusty or wet areas, the C-21 should be mounted in the Eco Sensors EE-1 Environmental Enclosure which protects it from these hazards.

CALIBRATION

The instrument indicates red at high levels of VOC gases and vapors. The C-21 is broadly sensitive to most VOCs, but its response is different for each one. To calibrate for a specific gas, a chemical laboratory is required. The procedure detailed in our Tech Note C-100. The perchloroethylene calibration ("perc" or dry cleaning fluid) is shown on the reverse side of this instruction sheet.

BATTERY OPERATION

To investigate a VOC leak, or to do field research, the instrument may be unplugged from the AC adapter and operated from its internal rechargeable battery for about 2 hours (This will not work on initial operation. The battery will require about 10 hours of charging which happens automatically whenever the instrument is being powered by the AC adapter).

ALARM

The audible alarm (buzzer) is normally triggered when the first red segment of the LED is lit. During warm-up of the instrument the sensor will read high for 1-2 minutes and the alarm will actuate unless it has been turned off.

The alarm set-point, which is the same set-point as for the internal relay contacts, can be changed through resetting the 8 toggle DIP switch found on the circuit board. This switch allows reconnecting the set-point across any of the top 8 bars of the LED display. Switch number 1 connects to the top red bar, all the way down to switch 8 controlling through the third green bar from the bottom of the display. Please note that no more *than one* switch should be *down* (on) at a time. If no switch is on, the alarm and internal relay will not work.

Normally, the third switch, corresponding to the first red bar, is on. This switch can be shut off using a pen or screwdriver actuating it through the upper middle hole in the back plate. When this is done, neither the alarm nor the internal relay contacts will function.
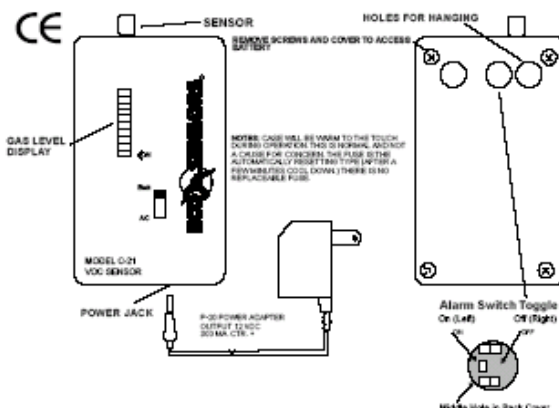
OUTPUTS TO EXTERNAL EQUIPMENT

The C-21 has two output circuits for external measurements and controls via the accessory plug. They are (refer to drawing on the reverse side of this instruction sheet):

Low powered (transistor) relay that will switch up to 30 volts at 130 mA directly, or it can drive an external power-handling relay that has its own coil power supply. This relay closes when the buzzer actuates because it is programmed by the same DIP switch that controls the buzzer.

0-2 volts DC output that increases as the VOC level increases. The first red bar on the LED bargraph corresponds to an output of one volt. The output is not linear, however. It is logarithmic (See output table, reverse side of this sheet). This DC output can be used to drive data loggers such as the Eco Sensors model DL-2 for PCs, a digital voltmeter for remote readout, or the Eco Sensors RAP-7800 Remote Access Panel. The RAP Panel has a 90 db alarm, a pulsating red strobe alarm light, and a 4-20 mA output loop to connect to a building control system (BCS). For RAP systems be sure to order the C21 with an interface terminal block.

USE IN VEHICLES

The C-21 may also be used in cars and trucks, or wherever there is 12 volts DC available. A cigarette lighter adapter should be purchased for this purpose from an electronics store. Make sure the plug selected fits our jack (2.5 mm) and that it is configured for center pin = +. Radio Shack has several models that work such as their part number 270-029. For vehicular use, the instruments panel switch should be in the AC position.

Vehicular use includes charging the battery in the C-21, checking for leaks in solvent containers, inspection of gasoline station and vehicle maintenance areas, and environmental checking of roadside hazards and spills.

SERVICE AND MAINTENANCE

The battery and the sensor are the only user serviceable parts of the instrument. While they should last 3-5 years, it is good practice to replace them annually.

Battery The nickel cadmium (NiCad) battery (9 volt snap-on connector) generally does not fail suddenly. After about a year, its performance will gradually decline. The battery replacement is Eco Sensors part number XB-C2. NiCad batteries are also available in local electronics stores such as Radio Shack (part number 23-526). Both NiCad and NIMH batteries will work, and both 7.2 volt (6 cell) and 8.4 volt (7 cell) models will work. The higher voltage version has a somewhat longer discharge life, but the lower voltage version will charge more efficiently if the AC adapter is only putting out 12-13 volts (most "12 volt" AC adapters, like our model P-20, put out about 15 volts under load). *Do NOT attempt to use alkaline or other non-chargeable batteries. The non-rechargeable batteries will overheat and destroy the instrument, voiding the warranty.*

The battery may be replaced by disconnecting the AC adapter and removing the back of the instrument. Exchange the batteries being careful to put the new battery in exactly where the old one was and to replace the protective felt material surrounding it.

Sensor If the instrument no longer responds to gases and vapors, the likely cause is sensor failure. The replacement sensor is the Eco Sensors part number SE-4.

AC Adapter For use in North America and other areas with the "American System" of 120 V 60 HZ, the Eco Sensors P-20 adapter should be used. For other areas adapters should be purchased locally that fit local wall sockets and conform to local codes. The output should be 12 volts DC unregulated, 300-500 mA. The plug to our instrument should fit a 5.5/2.5 mm socket with the center pin +. For further details see our Tech Note P-101.

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SPECIFICATIONS

Sensor: Heated metal oxide semiconductor.
Sensitivity: First responds at a few ppm for many VOC gases and vapors. Alarm typically sounds at about 50 ppm.
Response time: Within one minute of when gas reaches the sensor.
Audio alarm level: Approximately 80 db.
Temperature and humidity range: 0-40 deg C and 0-80% relative humidity.
Supply voltage required: 12 volts DC, 200 mA.
Battery life: Over 2 hours per charge.
Size of instrument: 85 X 35 X 60 mm (3 1/4" X 1 3/8" X 2 3/8").
Weight of instrument: 140 grams (5 oz.).
Shipping weight of instrument and adapter: about 2/3 kg. (1 1/2 lbs.)

SAFETY FEATURES

Enclosure: Self-extinguishing ABS plastic.
Sensor: Heated element is flame arrestor protected.
Electrical: (a) Circuits operate at 24 volts, 250 mA, or less with no high capacity inductors or capacitors. (b) Self-resetting fuse to protect against excess input current flow. (d) Overvoltage protection diode barrier to protect against supply voltage surges, spikes, overvoltage, and reverse polarities.

PRECAUTIONS

- Allow at least 5 minutes warm-up.
- Read all instructions in this manual.
- Keep instrument dry. Never let water or other liquids into the sensor.
- Do not drop the instrument or subject it to continuous vibration.
- Do not store in high levels of dust.
- Do not clean the instrument with cleaning chemicals or solvents. Clean it with a damp cloth.
- Do not operate near heavy aerosols (spray) usage or where oxygen is being administered.
- Call a qualified electrician if you have any doubts about voltages, currents, electrical practice, etc.

WARRANTY

This product is warranted against defects in materials and workmanship for one year following the date of purchase by the original owner. This warranty does not include damage to the product as a result of misuse, accident, damage, modifications or alterations, and it does not apply if the instructions in this manual are not followed.

If a defect develops during the warranty period, Eco Sensors at its election will repair the instrument or replace it with a new or reconditioned model of equivalent quality. In the event of replacement with a new or reconditioned instrument, the replacement unit will continue the warranty of the original unit.

To return the instrument contact your distributor, or call Eco Sensors at (800) 472-6626 or e-mail at sales@ecosensors.com to receive return instructions and a Return Goods Authorization (RGA) number.

Except as provided herein, Eco Sensors makes no warranties express or implied, including warranties of merchantability and fitness for a particular purpose. Eco Sensors shall not be liable for loss of use of the instrument or other incidental or consequential damages, expenses or economic low, or claims for such damage or economic loss.

This warranty gives you specific legal rights and you may also have other rights which vary from state to state.

RECORD YOUR SERIAL NUMBER HERE _____

KEEP THIS MANUAL AND WARRANTY FOR YOUR RECORDS.

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For brochures, application and tech notes, and other useful information, visit our extensive website at www.ecosensors.com. E-mail us at sales@ecosensors.com.

Response Data and Wiring Diagram on the next page.

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Eco Sensors Model C-21

RESPONSE RANGES FOR SOME COMMON VOCs

	First detects	Alarm (First red bar)	TLV*
	ppm	ppm	ppm
Acetone	4-5	20-25	750
Benzene	5-10	25-50	10
Diacetone alcohol	5-10	25-50	50
Formaldehyde	1-5	15-25	0.1
Methylene chloride	8-10	40-50	50
Methyl ethyl ketone	3-5	15-20	200
Perchloroethylene	5	50	50
Toluene	3-5	15-25	50
Trichloroethylene	10-20	50-100	50

*Threshold Limit Value. Average estimate of government industrial hygienists for repeated worker exposure.

DISPLAY CALIBRATION FOR "PERC"
(Partial calibration for perchloroethylene, the common dry cleaning fluid.)

LED Display	Concentration
	ppm
All green	20
All yellow	40
One red	50
Two red	100
All red	140

C-21 OUTPUT CIRCUITS
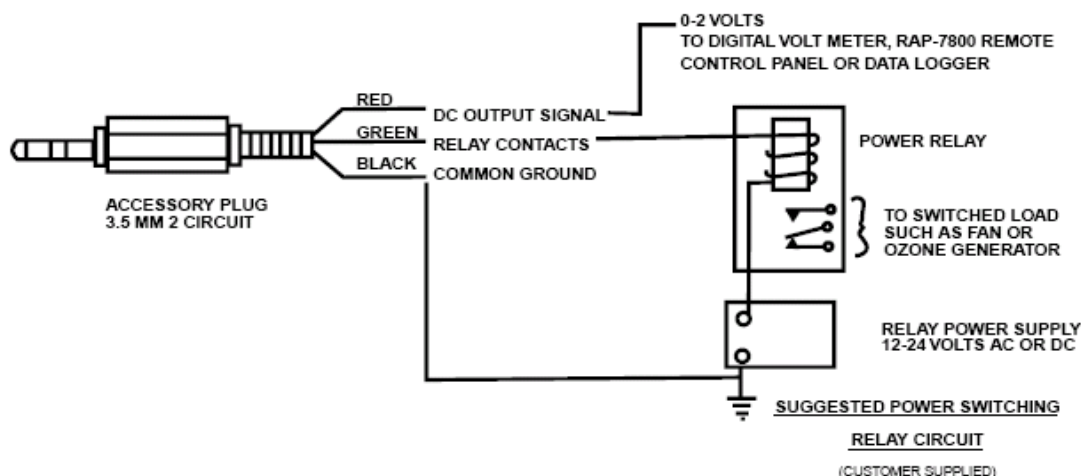
The C-21 internal relay is a "dry contact" FET device. It will handle up to 30 volts AC or DC at up to 130 ma so it will switch low voltage alarms directly. For switching power loads an intermediate relay and power supply should be used such as shown above.

RECOMMENDED ACCESSORIES

EE-1 Environmental Enclosure For dust and water protection in industrial and agricultural environments and where the public may be near the instrument. 120 x 180 x 90 mm (5"x 7"x 3") with a clear polycarbonate gasket front cover.

DL Series Data Loggers Tiny battery-operated data loggers record data for later analysis in PCs.

RAP-7800 Remote Alarm Panel In rugged PVC enclosure. Feature 90 dB audio alarm, red alarm strobe light, 4- 20 mA analog signal loop (for building control systems), and optional digital readout.

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ECO SENSORS, INC.

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TECH NOTE B-102

Response Ranges for some Common VOCs

For Models C-11, C-12, C-20 and C-21

Our C-11, C-12, C-20 and C-21 VOC monitors have the same responses and for some common VOCs their responses are:

	First Detects (ppm)	Alarms (ppm)	TLV*(First Red Bar) (ppm)	Recommended for This Chemical
Acetone	4-5	20-25	750	Yes
Benzene	5-10	25-50	10	No
Diacetone alcohol	5-10	25-50	50	Yes
Formaldehyde	1-5	15-25	0.1	No
Methylene chloride	8-10	40-50	50	yes
Methyl ethyl ketone	3-5	15-20	200	Yes
Perchloroethylene	5	50	50	Yes
Toluene	3-5	15-25	50	Yes
Trichloroethylene	10-20	50-100	50	Yes

*Threshold Limit Value. Average estimate of government industrial hygienists for repeated worker exposure.

Our instruments are very good at early warning in semi-quantitative terms, and for follow-up leak tracking, but they are not designed or sold as specific gas analyzers.

Tech Note B-102 (Revised 5/99)

Works\C-20\B-102A

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Mercury Monitoring

Jerome 431-X

The Jerome 431-X Mercury Vapor Analyzer uses a gold film sensor for the detection and accurate measurement of toxic mercury vapor in the air.

A portable hand-held unit, the Jerome 431-X can easily be carried to locations of mercury concerns. Simple, push-button operation allows users to measure mercury levels in just seconds. The range of the 431-X is from 0.000 to 0.999 mg/m3 Hg. The gold film sensor is inherently stable and selective to mercury, eliminating interference common to ultraviolet analyzers, such as water vapor and hydrocarbons.

The 431-X includes features not available in older Jerome models. When attached to either a data logger or computer, the analyzer automatically regenerates the sensor when it becomes saturated and then resumes sampling. An improved film regeneration circuit makes the sensor last even longer.

Features	*Portable, rugged and easy to operate* *13 second response* *Automated sample cycle* *Inherently stable gold film sensor* *Operates up to six hours on fully charged nickel-cadmium batter* *Digital display in either mg/m3 or ng* *One year limited parts and labor warranty*
Applications	*Mercury surveys* *Spill response* *Hazardous waste sites* *Mercury exclusion tests*
Specifications	*Accuracy: +/- 5% at 0.100 mg/m3 Hg* *Sensitivity: 0.003 mg/m3 Hg* *Range 0.000 to 0.999 mg/m3 Hg* *Precision: 5% relative standard deviation at 0.100 mg/m3 Hg* *Environmental Operating Range: 0-40 degrees C. non-condensing, non-explosive* *Response Time: Sample mode - 13 seconds; Survey mode - 4 seconds* *Flow Rate: 750cc/min.* *Weight: 7 pounds* *Dimensions: 6"W × 13"L × 4"H* *Case Design: Enform* *Power Requirements: 115VAC or 230VAC, 115 watts maximum*

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ENGINEERING DESIGN FILE

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Vendor GAC Estimates (Flanders Filters)

	0 hour	3 hour	6 hour	12 hour	24 hour
	concentration (ppm)				
Tetrachloroethene	335	185	103	31	3
1,1,1 trichloroethane	195	108	60	18	2
Trichloroethene	1019	718	505	251	69
Mercury	89	61	42	19	4

Adsorption capacities per given concentrations, grams of contaminated/100grams of carbon (Max capacities)

Tetrachloroethene	65	62	59	55	54
1,1,1 trichloroethane	32	30	27	23	20
Trichloroethene	50	47	44	41	35
Mercury	2.7	2.7	2.7	2.7	2.7

My recommendation for changing out the filters is based on the concentration of these 2 contaminates sent to me by T.J. The first change out should take place after the sixth hour of operation, the second change out should take place after the fourteenth hour of operation.

These change out times are based on $24 \times 24 \times 12$ in. filters, the carbon should be impregnated with 2% KI and operating at 250CFM.